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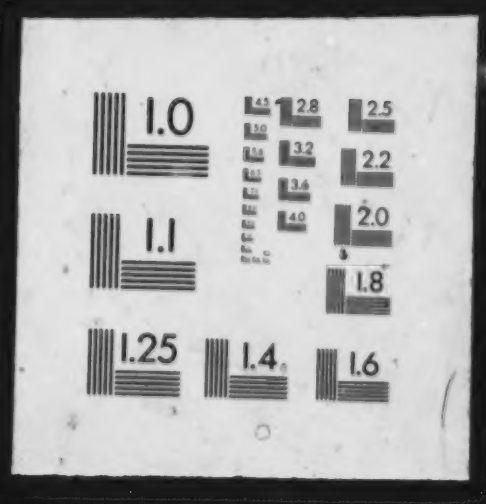

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Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC (Volatile Organic Compounds) and VHAP (Volatile Hazardous Air Pollutants)

(U.S.) Environmental Protection Agency
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16. ABSTRACT

EPA has developed a Protocol for Generating Unit-Specific Emission Estimates fir Equipment Leaks of VOC and VHAP. The protocol provides several methods for estimating emissions from equipment leaks. These methods range from the application of average emission factors for the equipment component inventory to the use of bagging data for generating unit-specific leak rate/screening value correlations. In addition, the protocol provides technically sound methods of source screening and mass emissions sampling (bagging). The document will help facitilies generate accurate plant-specific equipment leak emissions.

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Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP

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Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP

Emission Standards Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

October 1988

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GLOSSARY

Censored source - a source whose screening value is known to be above 100,000 ppmv but whose actual screening value is unknown.

Emission factor - the per component mass emission rate applicable to populations of sources, not individual component measurements.

Inaccessible source - a component which cannot be reached because it is beyond the reach of a 6-foot ladder.

Leak definition - monitoring instrument reading selected as the trigger value for initiating some action such as maintenance; e.g., 10,000 ppmv is the leak definition used by EPA.

Leak frequency - the percentage of sources (a particular equipment type and service) determined to be leaking based upon a chosen leak definition.

Leak rate - see mass emissions rate.

Leaking emission factor - the per component mass emission rate associated with the population of sources with screening concentrations at or above the leak definition.

Leaking source - a source whose screening concentration is greater than or equal to 10,000 ppmv.

Mass emissions rate - the quantity of volatile organic compound(s) released to the atmosphere in terms of total mass per unit time.

Monitoring instrument - portable hydrocarbon analyzer meeting the performance specifications given in Method 21.

Non-leaking emission factor - the per component mass emission rate associated with the population of sources with screening concentrations less than the leak definition.

Non-emitting source - a source whose screening value is 0 ppmv; a zero emission rate is assumed.

Non-leaking, emitting source - a source whose screening concentration is greater than 0 ppmv but less than 10,000 ppmv.

Screening value - raw monitoring instrument reading.

Screening concentration - the screening value (raw instrument reading) corrected by the appropriate response factor.

Unsafe-to-monitor equipment - equipment that exposes monitoring personnel to an immediate danger while screening the equipment.

EF = average emission rate per source

EF_1 = average emission rate per leaking source

EF_2 = average emission rate per non-leaking emitting source

X_{1i} = measured emission rate for the ith leaking source

X_{2i} = measured emission rate for the ith non-leaking emitting source

$\bar{X}_2$ = average measured emission rate for non-leaking emitting sources

N_1 = number of leaking sources

N_2 = number of non-leaking emitting sources

N_3 = number of non-emitting sources

N = total number of sources (including inaccessible sources)

n_1 = number of bagged leaking sources

n_2 = number of bagged non-leaking emitting sources

s_2^2 = estimate of the variance of the emission rates of the non-leaking emitting sources

$$= \sum_{i=1}^{n_2} (X_{2i} - \bar{X}_2)^2/(n_2 - 1)$$

y_{1i} = measured emission rate for the ith leaking source

y_{2i} = measured emission rate for the ith non-leaking emitting source

y_{1ai} = predicted emission rate for the ith leaking source screened <100,000 ppmv

y_{1bi} = measured emission rate for ith censored source

$\bar{y}_1$ = average predicted emission rate for leaking sources

$\bar{y}_2$ = average predicted emission rate for non-leaking emitting sources

$\bar{y}_{1a}$ = average predicted emission rate for leaking sources screened <100,000 ppmv

$\bar{y}_{1b}$ = average measured emission rate for censored sources

N_{1a} = number of leaking sources screened, <100,000 ppmv

N_{1b} = number of censored sources

n_{1b} = number of bagged censored sources

s_{y1}^2 = variance of the predicted emission rates of the leaking sources

$$= \sum_{i=1}^{N_1} (y_{1i} - \bar{y}_1)^2/(N_1 - 1)$$

s_{y2}^2 = variance of the predicted emission rates of the leaking sources screening <100,000 ppmv

$$= \sum_{i=1}^{N_2} (y_{2i} - \bar{y}_2)^2/(N_2 - 1)$$

s_{y1a}^2 = variance of the predicted emission rates of the leaking sources screening <100,000 ppmv

$$= \sum_{i=1}^{N_{1a}} (y_{1ai} - \bar{y}_{1a})^2/(N_{ia} - 1)$$

s_{y1b}^2 = variance of the measured emission rates of the censored sources

$$= \sum_{i=1}^{n_{1b}} (y_{1bi} - \bar{y}_{1b})^2/(n_{ib} - 1)$$

The symbol t is the value of the normal deviate corresponding to the desired confidence probability. If the number of bagged sources, n, is greater than or equal to 50 then the value of t approaches 1.96. If the sample size is less than 50, the percentage points may be taken from Student's t table with (n-1) degrees of freedom. The t distribution holds exactly only if the emission rates are normally distributed. Moderate departures from normality do not affect it greatly.

FOREWORD

The EPA's protocol for estimating equipment leak emissions is the result of detailed information gathering and data analysis. The protocol was written to provide a thorough understanding of acceptable approaches to generating process unit-specific emission estimates. In preparing this document, EPA has encouraged industry experts and trade association representatives to comment on the document's content. Chief among these contributors has been the Chemical Manufacturers Association (CMA), who has written a guidance document similar to this EPA protocol.

The CMA document is consistent with this guide. Both documents present acceptable approaches to generating emission estimates. Minor differences that exist between the two documents should not affect the acceptability of the emission estimates, provided the approaches to generating acceptable emission estimates are thoroughly understood. The CMA protocol includes a provision for the addition of bagging data from a single process unit to the EPA correlation curves to modify the leak rate/screening value correlation. While the EPA agrees with the technical premise that additional data could be added to the existing database, the Agency believes that, for practical reasons, this approach could create interpretation problems for control agencies. Therefore, the Agency does not support this approach. Currently, EPA is working with CMA to expand the existing database of equipment screening and bagging data. Ultimately, the Agency will consider the addition of the data currently being collected to the existing database. This effort may provide a better understanding of the magnitude of equipment leaks and appropriate controls for them. The EPA will consider appropriate modifications to this protocol when additional data collected during this interim period are analyzed.

1.0 INTRODUCTION

The purpose of this document is to present standard protocols for estimating mass emissions from equipment leaks. The EPA's interest in developing standard protocols is to assist states and industry in their efforts to estimate equipment leak emissions. Emission estimates are being developed for a variety of purposes, including permitting, inventories, and for the Superfund Amendments and Reauthorization Act (SARA).

The EPA previously developed equipment leak emission factors in previous work supporting standards. These factors represented emissions from typical facilities and were used to develop industry-wide emission estimates. The EPA's standards-setting process will continue to rely upon the average emission factors for industry-wide estimates. However, those estimates do not yield the accuracy that facilities are looking for today; therefore, there is now a need for more accurate emission estimating techniques.

Recognizing that the significance of our protocols is in providing a consistent approach to data collection and emissions estimates, EPA believes there is need for certain minimal requirements in any protocol. Our desire is to develop standard protocols for general use in generating unit-specific emission estimates for permitting and inventories.

This document describes methodologies the EPA considers appropriate for development of unit specific emission estimates for equipment leaks of organic compounds: volatile organic compounds (VOC) and volatile hazardous air pollutants (VHAP). Estimates generated using this protocol would be specific only to process units (or groups of sources) for which an estimate was made. EPA has made provision for extending such estimates beyond the limits of that group of sources.

Five methods for estimating emissions from equipment leaks from a specific chemical processing unit are included in the protocol:

- Average emission factor method;
- Leak/no-leak emission factor method;
- Three-strata emission factor method;
- Application of EPA correlations; and
- Development of new correlations.

They range from simply applying accurate equipment counts to the EPA's average emission factors to the more complex project of developing unit-specific correlations of mass emission rates and screening values.

All methods start with obtaining an accurate identification and count of equipment to be included in the emission estimate. The equipment counts can simply be used with the EPA's previously developed emission factors. The next step in complexity and refinement is the use of a portable organic analyzer to find the number of leaking and nonleaking sources. Leaking and nonleaking emission factors previously developed by the EPA can then be applied to generate the emission estimate.

A final refinement in a method employing discrete emission factors is that of applying emission factors to represent three different ranges of screening values. This has been called the stratified emission factor approach, or the three-strata approach. Applying the stratified emission factors requires more rigorous measurement of organic vapor concentrations with a portable instrument because actual concentration readings must be recorded instead of noting whether a piece of equipment is classified as leaking or not leaking.

The remaining two methods make use of correlation equations relating mass emissions to organic concentrations measured with a portable organic analyzer. The EPA's previously developed correlations are offered for use, and finally, if a process unit's emissions are statistically different from those represented by the EPA's correlations, provision is made for development of correlations specifically for that process unit.

Guidance and recommendations are offered for statistical analyses and for gathering the data required to execute the methods. The information is provided in the following major sections of this protocol:

- Section 2.0 Emission Estimate Development;
- Section 3.0 Source Screening;
- Section 4.0 Mass Emissions Sampling.

Section 2.0 details the types of data needed for making emissions estimates and how that data is to be applied. Sections 3.0 and 4.0 offer more detail on collection of data using a portable organic analyzer and using a technique known as "bagging," in which an enclosure is made around a potential leak point and emissions are actually measured. Additional reference material is included in the Appendices.

2.0 DEVELOPMENT OF EMISSION ESTIMATES

2.1 INTRODUCTION

In this section, five methods for estimating VOC and VHAP emissions from equipment leaks in chemical processing units are described. The methods increase in complexity and in the amount of data collection and analysis required. However, all five methods require some data collection, data analysis, and/or statistical evaluation. The five estimation methods and the options available for collecting and analyzing the data are shown in Figure 2-1. As the flow chart shows, the methods increase in rigorousness and complexity. The first method, the average factor method, is the least complex and demanding and the last method, developing site specific correlations, is the most complex and demanding. The end product of each of the procedures described is an emissions inventory for equipment leaks by type of equipment and by service (i.e., light liquid, gas, heavy liquid).

2.2 USE OF THE EPA'S AVERAGE EMISSION FACTORS

All of the methods require an accurate count of equipment components by type of equipment and by service. The most basic approach for estimating emissions merely requires application of average emissions factors developed by EPA to the equipment counts for the unit. EPA's average emission factors are shown in Table 2-1. The product of the emission factor and the number of equipment components yields the emission rate per source type, and the emission rates for all source types are summed to generate the unit-specific emission estimates.

The method EPA used for development of emission factors for individual equipment leak emission sources was described in reports on the Petroleum Refinery Assessment Study.[10,11] In this study, "screening" data were gathered using a portable organic vapor analyzer, and mass emissions were measured by enclosing individual pieces of equipment with bags or tents and measuring the organic material emitted.

These data permitted the development of leak rate/screening value correlations and emission factors for sources in petroleum refineries. Subsequently, EPA coordinated the SOCMI 24-unit Study,[15] a study of 24 individual chemical process units representing a cross-section of the SOCMI

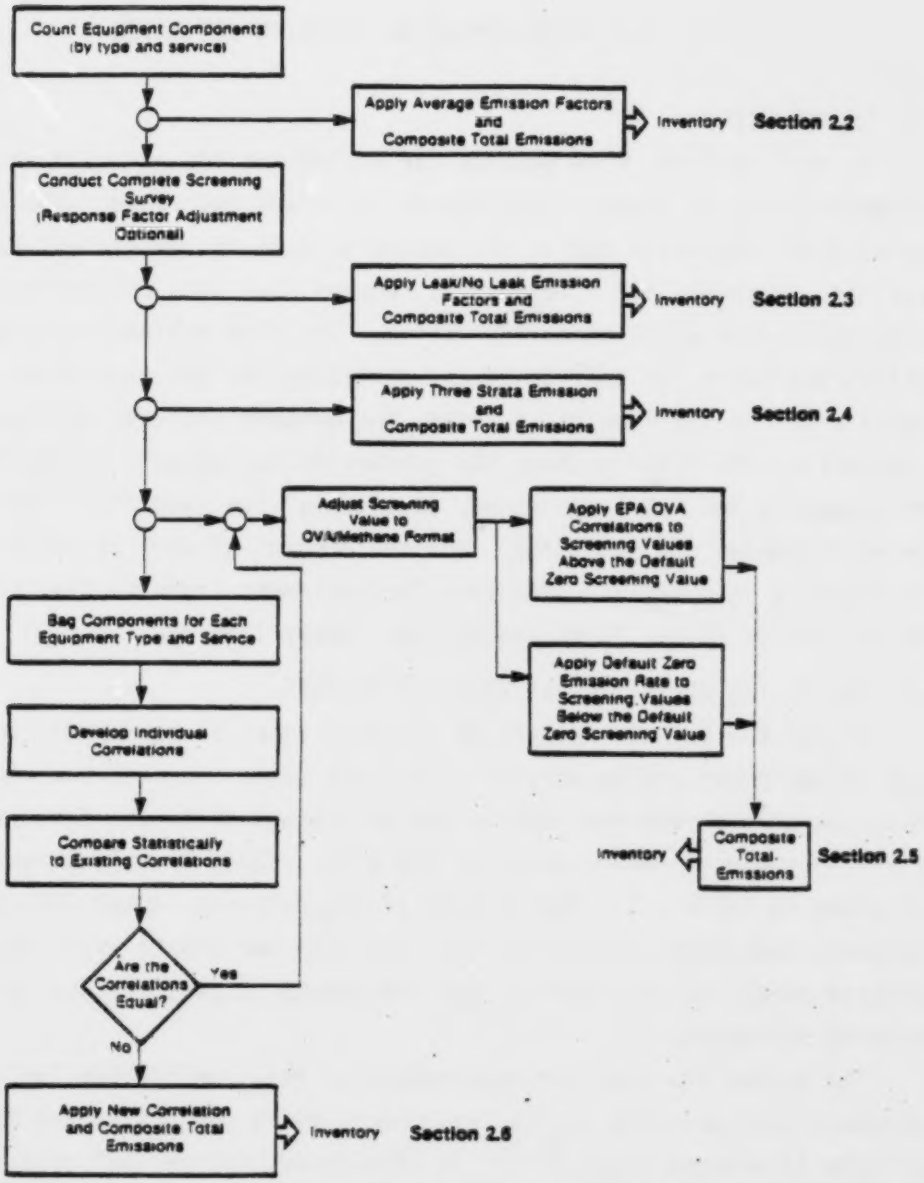

Count Equipment Components (by type and service)
Apply Average Emission Factors and Composite Total Emissions
Inventory
Section 2.2
Conduct Complete Screening Survey (Response Factor Adjustment Optional)
Apply Leak/No Leak Emission Factors and Composite Total Emissions
Inventory
Section 2.3
Apply Three Strata Emission and Composite Total Emissions
Inventory
Section 2.4
Adjust Screening Value to OVA/Methane Format
Apply EPA OVA Correlations to Screening Values Above the Default Zero Screening Value
Apply Default Zero Emission Rate to Screening Values Below the Default Zero Screening Value
Bag Components for Each Equipment Type and Service
Develop Individual Correlations
Compare Statistically to Existing Correlations
Inventory
Composite Total Emissions
Section 2.5
Are the Correlations Equal?
Yes
No
Apply New Correlation and Composite Total Emissions
Inventory
Section 2.6

Figure 2-1. Strategy for Estimating Emissions from Equipment Leaks

TABLE 2-1. AVERAGE EMISSION FACTORS FOR FUGITIVE EMISSIONS

Equipment	Service	Emission Factor (kg/hr/source)
Valves	Gas	0.0056
	Light Liquid	0.0071
	Heavy Liquid	0.00023
Pump Seals	Light Liquid	0.0494
	Heavy Liquid	0.0214
Compressor Seals	Gas/Vapor	0.228
Pressure Relief Seals	Gas/Vapor	0.104
Flanges	All	0.00083
Open-Ended Lines	All	0.0017
Sampling Connections	All	0.0150

population, and a six-unit Maintenance Study.[14] As a result of these chemical process unit studies, leak rate/screening value correlations and emission factors were generated for valves in gas/vapor service in SOCMI. Leak rate/screening value correlations were also generated for light liquid valves and light liquid pumps in SOCMI, but industry average emission factors were not developed.

2.3 THE LEAK/NO-LEAK APPROACH

The second method offers some refinement over the average emission factor method, thereby allowing some adjustment to individual unit conditions and operation. This method and all the remaining methods require screening of all equipment to be included in the inventory using a portable analyzer. Equipment that is dangerous to screen may be omitted from the set of equipment components to be screened. Their emission rates may be estimated using the EPA's average factors presented in Table 2-1.

Insulated equipment can be considered difficult-to-monitor equipment. The decision to remove insulation to facilitate screening is left to individual judgement. If insulation is not removed, the insulated component is assumed to leak at the same rate as a similar uninsulated component.

For flanges, a reduced number of components may be screened. Appendix E describes how to select the sample size for flanges. In compiling screening values for use in this technique (or any of those that follow), a response factor may be applied to correlate the screening values measured for the chemical in the line to the screening values observed in calibrating the instrument to another chemical. For a discussion of response factor adjustment, see Section 3.2.2.1.

The leak/no-leak approach to estimating emissions is based on the assumption of only two emission rates and two populations of equipment components: sources that "leak" (with screening concentrations greater than or equal to 10,000 ppmv) and sources that do not "leak" (with screening concentrations less than 10,000 ppmv).

The basis of this approach is as follows: when a group of sources leak, they leak at a certain emission rate on the average. Similarly, as a group, non-leaking sources have, on the average, a certain mass emission rate

associated with them. Thus, the overall emission estimate for a population of emission sources consists of two components: leaking source emissions and non-leaking source emissions.

Table 2-2 presents leaking and non-leaking emission factors previously determined by EPA for equipment leaks. EPA generated leaking and non-leaking emission factors using: 1) emission factors generated from empirical screening distribution data and leak rate/screening value correlations, 2) the leak frequencies associated with the emission factors, and 3) the percent of mass emissions associated with the leaking sources. The detailed procedure for generating leaking and non-leaking emission factors has been previously published in the "Additional Information Document" (AID)[13] for fugitive emission sources of organic compounds and is also described in a document entitled "Emission Factors for Equipment Leaks of VOC and HAP."[16]

The application of the leak/no-leak approach for estimating emissions is shown in the following example for a hypothetical chemical process unit.

Table 2-3 presents the data for this hypothetical process unit needed to apply the leak/no-leak procedure for estimating emissions. The first column shows the number of sources in the process unit by source type. The second column shows the number of sources with screening values greater than or equal to 10,000 ppmv (i.e., leaking sources). The percentage of sources leaking is shown in the third column. The emission estimates for this hypothetical process unit can then be computed using the leaking and non-leaking emission factors in Table 2-2. For example, three of the 47 pump seals in light liquid service were found to be leaking. Using the leak/no-leak approach, the emission estimate is generated:

(0.437 kg/hr/source)(3) + (0.012 kg/hr/source)(47-3),

or 1.84 kg/hr. The emission estimate per source for pumps in light liquid service could then be computed by dividing the unit-specific emission estimate by the equipment count. The last column in Table 2-3 shows the annual emission estimates by source type for the hypothetical unit.

While this example illustrates how total VOC emissions per source type are calculated, a similar procedure can be used to estimate emissions for a particular species in the line. For example, consider this same hypothetical case where the light liquid pumped contained 20 weight percent of Compound A.

TABLE 2-2. LEAKING AND NON-LEAKING EMISSION FACTORS FOR FUGITIVE EMISSIONS (kg/hr source)

Equipment	Service	Leaking (≥10,000 ppm) Emission Factor	Non-leaking (<10,000 ppm) Emission Factor
Valves	Gas[a]	0.0451	0.00048
	LL[b]	0.0852	0.00171
	HL[c]	0.00023[d]	0.00023
Pump Seals	LL	0.437	0.0120
	HL	0.3885	0.0135
Compressor Seals[e]	Gas	1.608	0.0894
Pressure Relief Valves	Gas	1.691	0.0447
Flanges	All	0.0375	0.00006
Open-Ended Lines	All	0.01195	0.00150

[a]The leaking and non-leaking emission factors for valves in gas/vapor service are based upon the emission factors determined for gas valves in ethylene, cumene, and vinyl acetate units during the SOCMI Maintenance Study. References 8 and 15.

[b]LL - light liquid service.

[c]HL - heavy liquid service.

[d]Leaking emission factor assumed equal to non-leaking emission factor since the computed leaking emission factor (0.00005 kg/hr/source) was less than non-leaking emission factor.

[e]Emission factor reflects existing control level of 60 percent found in the industry; control is through the use of barrier fluid/degassing reservoir/vent-to-flare or other seal leakage capture system.

TABLE 2-3. ESTIMATE OF "UNCONTROLLED" FUGITIVE EMISSIONS FOR A HYPOTHETICAL CASE

Source	Number Screened	Number Leaking	Percent Leaking	Computed Emission Estimate[a] (per Source) kg/hr/source	Annual[b] Emissions Mg/yr
Pump Seals					
Light Liquid	47	3	6.4	0.0391	16.1
Heavy Liquid	3	1	33.3	0.1385	3.6
Valves					
Gas/Vapor	625	19	3.0	0.0018	10.1
Light Liquid	1180	13	1.1	0.0026	27.2
Heavy Liquid	64	0	0	0.00023	0.1
Pressure Relief Valves					
Gas/Vapor	31	1	3.2	0.0978	26.6
Open-Ended Lines	278	9	3.2	0.0018	4.5
Compressor Seals	4	0	0	0.0894	3.1
Sampling Connections	70	-	-	0.0150	9.2
Flanges	2880	20	0.7	0.00032	8.1

[a]Based on values from Table 2-2, using EE = [LEF * PCL + NLEF * (100-PCL)]/100 where

EE = Emission Estimate (per Source)
LEF = Leaking Emission Factor
NLEF = Non-leaking Emission Factor
PCL = Percent of sources found leaking

[b]This hypothetical process unit is assumed to be in continuous operation, so it operates for 8,760 hours per year. Batch or campaign processes may operate fewer hours per year, so the annual emissions would be prorated to account for the hours the equipment contained the chemical.

The emission estimate for Compound A for light liquid pumps is computed by applying the weight percent (20 percent in this case) to the emission estimate generated above:

(0.20)(1.84 kg/hr) = 0.368 kg/hr.

As another example, consider the hypothetical case where the light liquid pumped contained only 80 weight percent VOC and Compound A accounted for 20 percent by weight. The emission estimate for Compound A for light liquid pumps is computed as:

(0.2/0.8)(1.84 kg/hr) = 0.460 kg/hr

In other words, compound A accounts for one-fourth of the total VOC emissions of 1.84 kg/hr. As before, emissions per source can be determined by dividing the estimate by the number of components involved. Emission factor estimates calculated in this manner may then be applied to the equipment counts (where the material in the process line contained 20 weight percent of compound A) to estimate emissions of compound A for that specific process unit.

2.4 APPLICATION OF STRATIFIED EMISSION FACTORS

Another approach to generating emission estimates involves a refinement of the leak/no-leak approach discussed above. The leak/no-leak approach is based on two emission rates and two populations (i.e., leaking and non-leaking sources). The stratified emission factor approach, on the other hand, is based on several population and emission factors spanning several discrete screening value ranges.

Screening values in the EPA SOCMI data base are distributed widely from 0 ppmv to over 100,000 ppmv. The mass emissions are correspondingly distributed. The stratified emission factor approach for estimating emissions segments this distribution into discrete intervals to account for different ranges of screening values. The following ranges are used:

- 0 - 1,000 ppmv;
- 1,001 - 10,000 ppmv; and
- over 10,000 ppmv.

Using data gathered during previous EPA studies, emission factors for each screening value range have been generated. These stratified emission factors represent the leak rates measured during fugitive emissions testing.

Their development incorporated the statistical methods used by the EPA in developing other emission factors. The emission factor for each discrete interval is presented in Table 2-4 by equipment type and service.

This method requires that screening of all equipment (except that which is hazardous to screen) be conducted in accordance with methods described in Section 3 of this report. All screening values must be recorded according to the applicable ranges. Then, as with the leak/no-leak approach, the total emission estimate is generated by applying the number of components in each screening value range to the appropriate emission factor and summing each subtotal. An example of this procedure, shown in Table 2-5, illustrates how to implement the stratified emission factor approach.

2.5 LEAK RATE/SCREENING VALUE CORRELATIONS

Mathematical correlations offer an additional refinement to estimating emissions from equipment leaks by providing a continuous function over the entire range of screening values instead of discrete intervals. The EPA has published correlations relating screening values to mass emissions rates. As shown in Appendix D, there are four correlations which can be applied to all equipment types and services. The EPA's correlations are based upon OVA measurements taken using Method 21. The instrument was calibrated to methane (see Method 21). Screening value measurements used with these published correlations should be in this same format. For example, if a TLV instrument calibrated to hexane were used to gather screening data, the data must be transformed to represent measurements gathered using an OVA, calibrated to methane, before using the published correlations. If a detector fails to meet Method 21 specifications or published transformations are not available, an instrument response curve must be developed to relate screening values to actual concentrations in the appropriate format (OVA/methane). Development of this screening value correction curve should be done in the laboratory before the detector is used in the field.

Another correction factor that can be applied to Method 21 and non-Method 21 instruments is the response factor. For many compounds, the instrument response is non-linear with increasing screening value. In terms of the basic leak/no-leak approach described in a previous section, a single

TABLE 2-4. STRATIFIED EMISSION FACTORS FOR EQUIPMENT LEAKS
(kg/hr/source)

Source	Service	Emission Factors (kg/hr/source) for Screening Value Ranges, ppmv		
		0-1,000	1,001-10,000	Over 10,000
Compressor seals	Gas/vapor	0.01132	0.264	1.608
Pump seals	Light liquid	0.00198	0.0335	0.437
	Heavy liquid	0.00380	0.0926	0.3885
Valves	Gas/vapor	0.00014	0.00165	0.0451
	Light liquid	0.00028	0.00963	0.0852
	Heavy liquid	0.00023	0.00023	0.00023
Flanges, connections	All	0.00002	0.00875	0.0375
Pressure relief devices	Gas/vapor	0.0114	0.279	1.691
Open-ended lines	All	0.00013	0.00876	0.01195

TABLE 2-5. ESTIMATE OF FUGITIVE EMISSIONS USING STRATIFIED EMISSION FACTORS FOR A HYPOTHETICAL CASE

Source	Number Screened	Number of Sources Screening (ppmv)			Computed Emission Estimate	
		0-1,000	1,001-10,000	Over 10,000	per Source Type[a] (Kg/hr)	per Source[b] (Kg/hr/source)
Compressor seals						
Gas/vapor	4	3	1	0	0.298	0.0745
Pump seals						
Light liquid	47	32	12	3	1.776	0.0378
Heavy liquid	3	1	1	1	0.485	0.1616
Valves						
Light liquid	1,180	1,020	147	13	2.81	0.00238
Heavy liquid	64	63	1	0	0.01472	0.00023
Flanges	2,880	2,600	160	20	2.20	0.00076
Pressure relief devices						
Gas/vapor	31	25	5	1	3.37	0.1087
Open-ended lines	278	236	33	9	0.427	0.00154

[a]Based on emission factors from Table 2-2, where $EE = (NL_1 * SEF_1) + (NL_2 * SEF_2) + \ldots$

EE = Emission Estimate

NL_1, NL_2, etc. = Number leaking in 1st range (0-1,000), Number leaking in 2nd range (1,001-10,000), etc.

SEF_1, SEF_2, etc. = Stratified emission factor for 1st range, stratified emission factor for 2nd range, etc.

[b]Computed Emission Estimate per source = Computed Emission Estimate per Source Type/Number Screened.

point response factor adjustment at the leak definition of 10,000 ppm is adequate. If, however, the correlations are to be used, the best estimate of screening concentration over the entire range is needed. Therefore, a correction for non-linear response must be made. This can be accomplished in the laboratory by generating a response curve.

The flow chart in Figure 2-1 shows a separate treatment of "zero" screening values. The function describing the correlation of leak rate and screening value becomes discontinuous for zero and near zero values. The correlation function mathematically predicts zero emissions for zero readings on the portable instrument. Empirically speaking, however, the EPA's data shows this prediction to be incorrect. Mass emissions have been measured from equipment showing no screening concentration above zero. The reason for this involves the detector accuracy. In the Refinery Assessment Study mass emissions corresponding to a screening value of 200 ppm or less could not be quantified because the accuracy limit of the detector was 200 ppm. To handle this discontinuity at the low end of the correlation, the EPA has derived a "default zero" screening value (8 ppm) and an associated mass emission rate for the screening values between zero and that default zero reading. These "default zero" values and emission rates shown below were derived as shown in Appendix F from mass emissions data gathered in chemical plants and the published leak rate/screening value correlations shown in Appendix D:

Equipment Type/Service	"Default Zero" Screening Value, ppm	Zero Screening Value Emission Rate (kg/hr/source)
Valves, gas	8	0.000033
Valves, light liquid	8	0.000451
Flanges	8	0.000093
Pumps and all other components	8	0.000039

These emission factors should be applied to equipment components screening between 0 and 8 ppm. The published correlations would be applied to all screening concentrations above 8 ppm. The total emissions estimate for equipment leaks is generated by totaling emissions estimates for all "default zeroes" and adding that total to the total estimates generated using the correlations. Appendix G presents an alternative methodology for generating unit-specific default zero emission rates.

2.6 UNIT-SPECIFIC CORRELATIONS

A process unit may develop its own correlations if leak rates are statistically different from EPA's rates. The steps involved in generating a unit-specific emissions estimate using correlations developed specifically for that unit are:

1. Gathering of mass emission data and calculation of mass emission rate (leak rate);
2. Development of leak rate/screening value correlations;
3. Statistical consideration of leak rate/screening value correlations;
4. Application of leak rate/screening value correlation to the empirical screening data; and
5. Prediction of emissions.

These steps are discussed individually in the following sections.

2.6.1 Generation of Mass Emissions Data

After complete screening of the process unit is done for all source types (except possibly flanges), selected sources can be bagged to measure the mass emission rate. The sources selected for mass emission measurement should be rescreened at the time of bagging. The mass emission rate determined by bagging and the rescreening value can then be used to validate the application of EPA's correlations to the process unit. Alternatively, the measurements can be used in development of leak rate/screening value relationships for that specific unit. The screening value can be affected by the portable screening instrument used and the gas used to calibrate the instrument. The EPA leak rate/screening value correlations are based on data gathered using an OVA instrument calibrated with methane.

If other instruments or calibration gases are used, then the screening value should be adjusted (using theoretical or empirical correction factors) to be equivalent to values measured using an OVA calibrated with methane prior to any comparisons to the EPA equations. Instrument readings above the saturation point of the detector must be bagged to quantify the emission rate.

The amount of leak rate testing (bagging) that should be done depends on the objective of the data collection. If one wishes to check the fit of EPA published equations to a particular process unit, as few as four leak rate measurements of a particular source type in a particular service may be

adequate. If it is desirable to develop new equations, 30 leak rate measurements should be obtained. Because of the inherent variability of leak rate/screening data, it is difficult to detect differences between correlations with fewer than 30 data pairs. However, the statistical goal is to generate estimates that are within 50 percent of the mean value with 95 percent confidence. If this statistical goal can be achieved with fewer data pairs, then fewer data pairs are acceptable.

Consider a hypothetical process unit having a large population of sources with screening values well distributed over the range of 0 to 100,000+ ppmv. To develop statistically valid leak rate/screening value correlations, mass emissions data must be collected from individual sources that have screening values distributed over the entire range. For each source type (i.e., valves, pumps, etc.) and service (i.e., gas, light liquid, etc.), a random sample of six sources should be chosen for bagging from each of the following screening value ranges:

Screening Value Range (ppmv)
1 - 100
101 - 1,000
1,001 - 10,000
10,001 - 100,000
> 100,000

If the maximum response of the screening instrument is 100,000 ppmv, then 20 or all (whichever is less) of the sources screened at 100,000 ppmv should be bagged. If six sources are not available in a particular screening value range, additional sources from the nearest range should be tested. If screening values greater than 10,000 ppmv are not found in the process, the following five groups can be used:

1 - 100 ppmv
101 - 300 ppmv
301 - 1,000 ppmv
1,001 - 3,000 ppmv
3,001 - 10,000 ppmv

Similar groupings can be developed if all sources in the unit screen less than 1,000 ppmv.

If a statistical determination is made that estimates within 50 percent of the mean value with 95 percent confidence can be achieved with fewer than 30 data pairs, the following bagging strategies are recommended:

SCREENING VALUE RANGE (ppmv)	TOTAL NUMBER OF LEAK RATE MEASUREMENTS			
	4	8	12	20
1 - 100	2	2	3	4
101 - 1,000		1	2	4
1,001 - 10,000		1	2	4
10,001 - 100,000	2	2	3	4
> 100,000		2	2	4

These groupings and recommended number of sources are given as guidelines. They are based on experience in measuring leak rates and developing leak rate/screening value equations. Other source selection strategies can be used if an appropriate rationale is given.

2.6.2 Development of Leak Rate/Screening Value Correlations

With appropriate mass emission data and screening values, leak rate/screening value correlations can be generated. Least-squares regression analyses are done for each source type/service, regressing the logarithm of the nonmethane leak rate on the logarithm of the screening concentration, according to

$$\text{Log (leak rate)} = B_0 + B_1 \text{ Log (screening concentration)},$$

where

B_0, B_1 = model parameters.

All analyses should be done using logarithms of both the leak rate and screening concentration. Confidence intervals should be calculated for the estimated equation (Reference 19, pages 28-31). A scale bias correction factor (Reference 20) is required in transforming the equation in the log-scale back to the original units. A statistician should be consulted unless one is familiar with this type of analysis. Bagged sources whose screening values are known to be above 100,000 ppmv but whose actual screening

values are unknown should not be used to fit the regression line described above. For those sources censored at 100,000 ppmv and which were not bagged, leak rates should be estimated from the average leak rate for those censored sources that were bagged.

2.6.3 Statistical Considerations of Leak Rate/Screening Value Correlations

The predictive equations resulting from the least-squares regression analyses discussed above must be statistically evaluated.

If new correlation equations are developed, they must be shown to be statistically different from the existing correlations developed during the refinery and SOCMI studies. If the new correlations are statistically different from the existing correlations, the new correlations may be used in the development of the unit-specific emission estimates for that specific class of sources. If not, the EPA's correlations should be used. The correlations can be compared graphically or mathematically.

2.6.3.1 Graphical Comparison of EPA vs. Other Correlations. If enough data are collected to develop a process specific leak rate/screening equation, then this equation should be compared to the published EPA equation. The EPA's predictive equation should be used unless the equation developed for the specific process unit is found to give significantly different estimates. This comparison can be done graphically by drawing the process specific equation on a graph of the EPA equation. Figure 2-2 (from Reference 14, page 66) is an example of such a graph.

A graphical comparison may also be made by plotting the leak rate/screening data from the process on a log-scale plot of the EPA equations. The log scale is preferred so that linear comparisons can be made. Figures 2-3 through 2-5 (from Reference 14, pages 57-62) show such plots of the EPA equations. The leak rate/screening value measurements used to develop the equations are also shown on the plots. These plots were developed from draft versions of the correlations. The correlations were refined when censored sources were included in modeling the leak rate/screening value relationships. Only small differences exist between the old and new models (see Reference 8, pages 14-18).

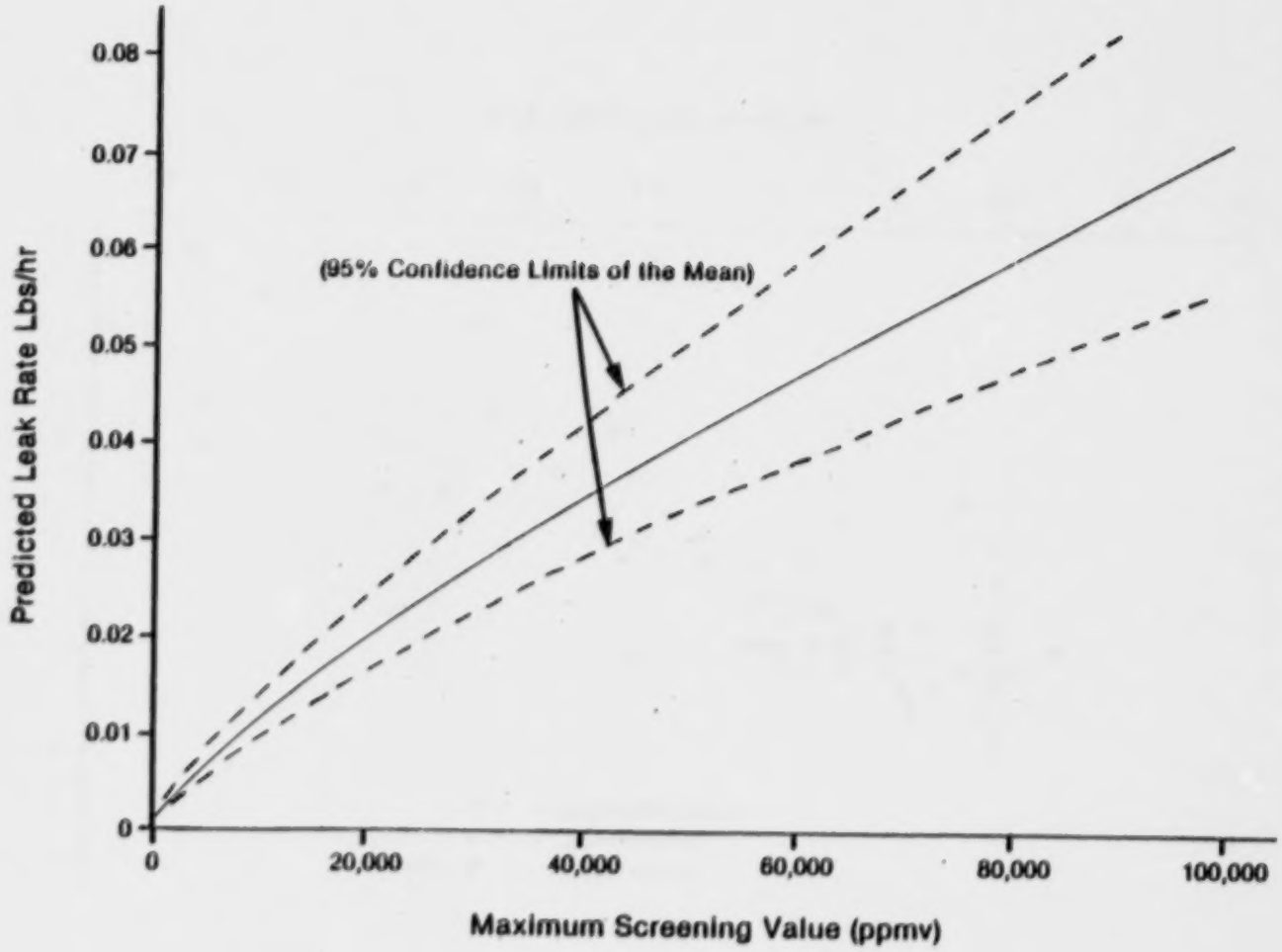


Figure 2-2. Modeled relationship - leak rate vs. OVA for valves in gas service.

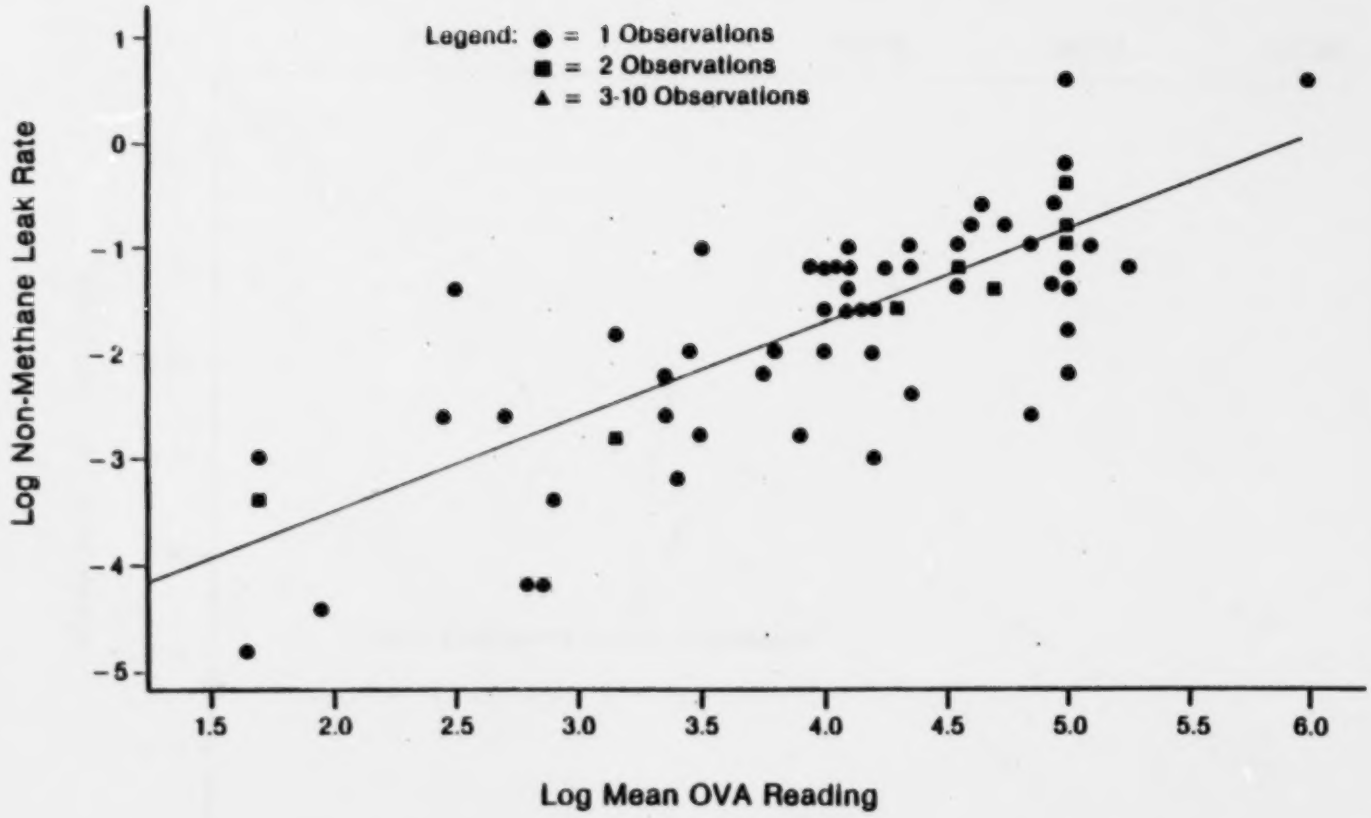


Figure 2-3. Log_{10} leak rate vs. log_{10} OVA reading for pump seals.

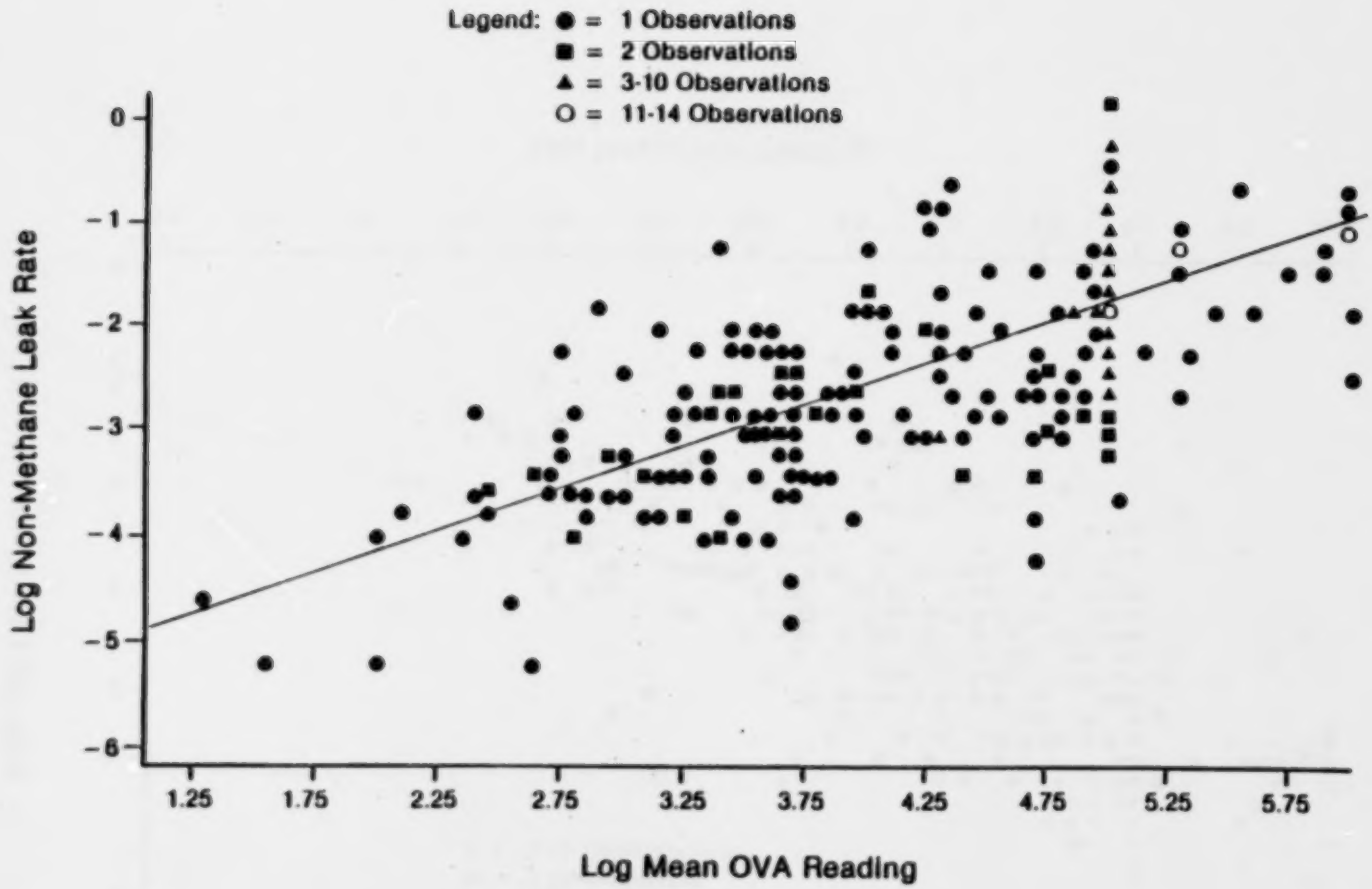


Figure 2-4. Log_{10} leak rate vs. log_{10} OVA reading for valves in gas service.

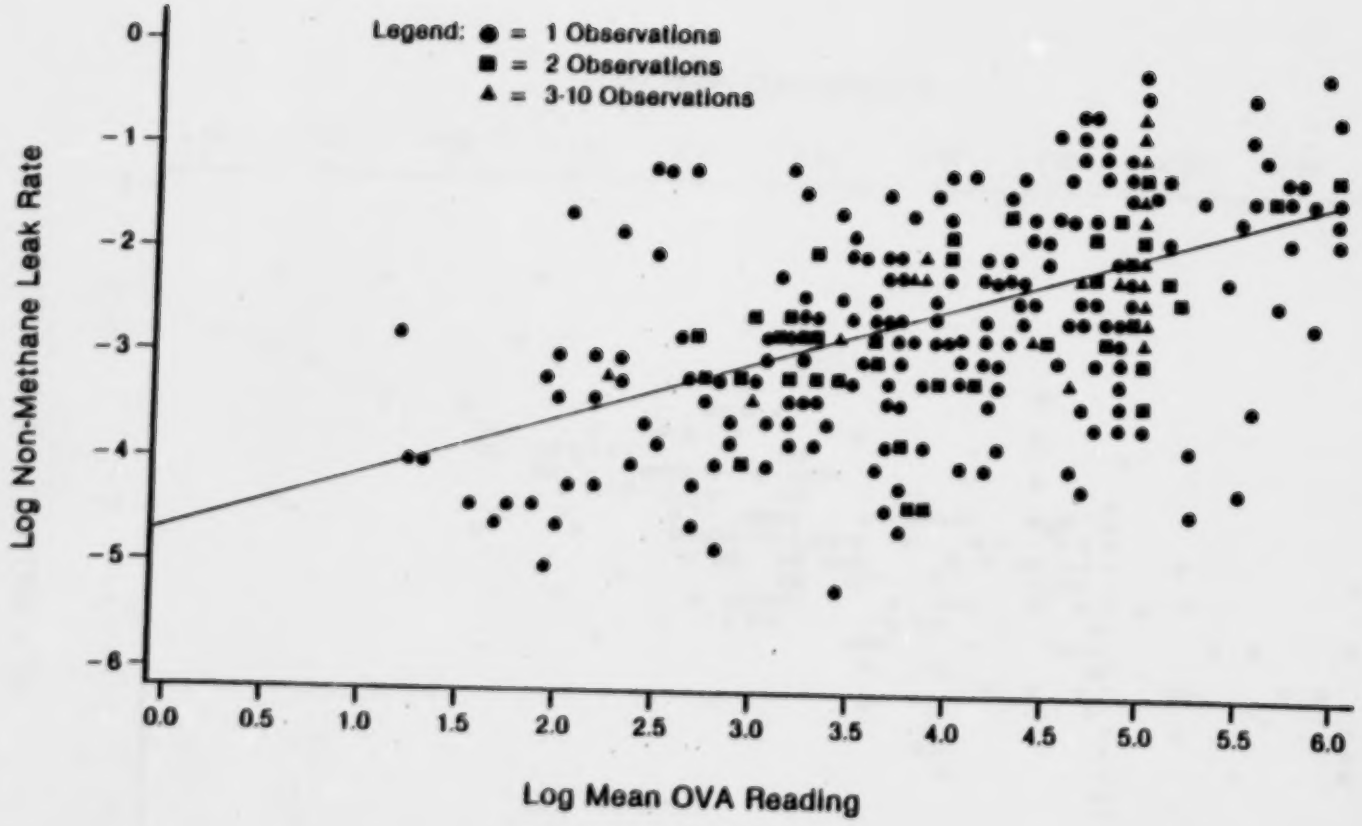


Figure 2-5. Log_{10} leak rate vs. log_{10} OVA reading for valves in liquid service.

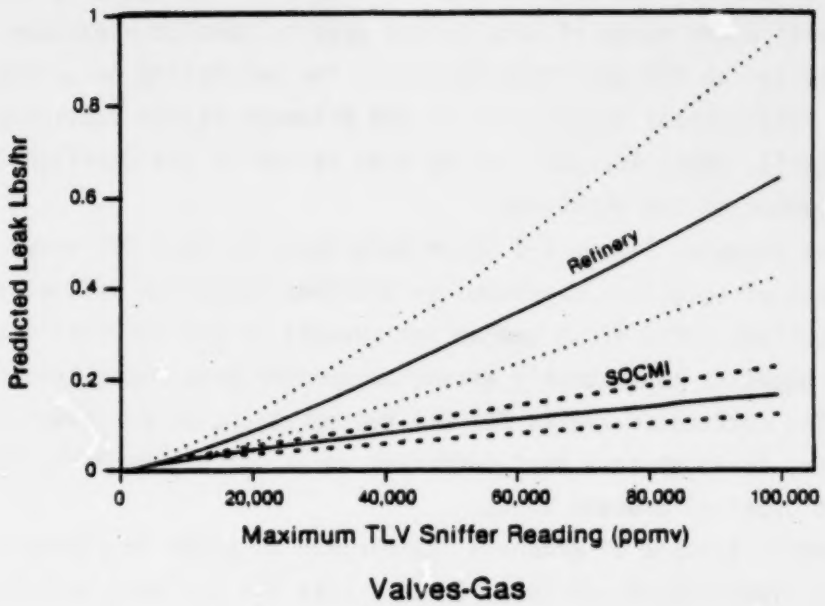
If the points fall on both sides of the line representing the equation and are within the range of data points used to develop equations, then it is reasonable to use the published equations for estimating emissions from the process. Statistical tests, such as the Wilcoxon Paired Replicate Rank test (Reference 21, pages 401-403) can be used to aid in the decision of reasonableness of the equations.

As an example, Figure 2-6 (from Reference 14, page 79) shows two comparisons of equations developed by EPA from Petroleum Refineries to the SOCMI equations. The first comparison (valves in gas service) shows the refinery equation consistently estimates greater leak rates throughout the curve. The confidence limits for the two equations do not overlap. For this comparison, it is obvious that different equations are required for the two different types of process units.

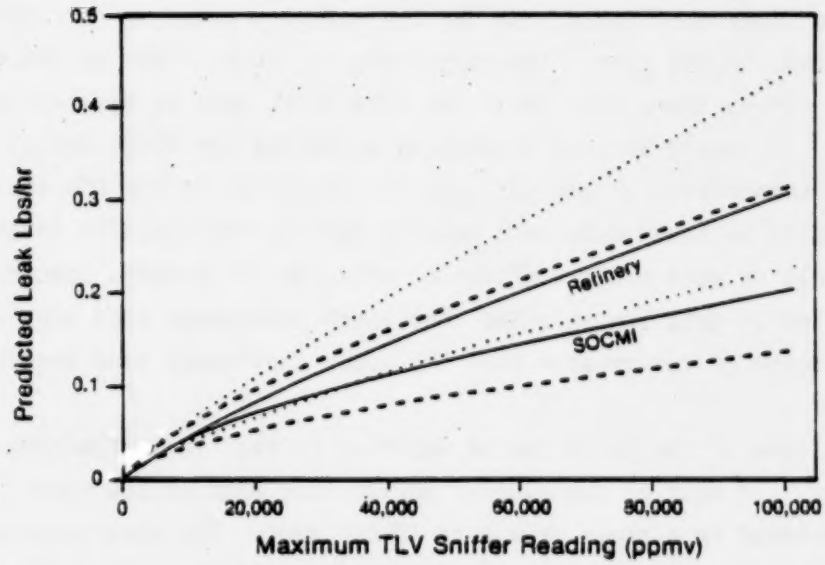
A second example of graphical comparison is shown in Figure 2-6 for valves in light-liquid service. In this case the refinery equation estimates greater leak rates than the SOCMI equation, but the refinery equation is within the confidence bands for the SOCMI equation. The SOCMI equation falls below the lower confidence band for the refinery equation for valves screening greater than 30,000 ppmv. The comparison is not as clear as the valves in gas service. Since there were about 300 data pairs used to develop the SOCMI equation, it should be used to develop estimates for SOCMI units.

For comparisons of process specific equations to the EPA equations there will usually be fewer data sets used to develop the specific equations. This will result in much wider confidence bands for the process specific equations. If 30 pairs of data are selected, the upper confidence band should be less than a factor of two greater than the upper confidence band predicted by the equation.

The form of the graph can be modified to facilitate the comparison of the equations. If most of the sources screen less than 10,000 ppmv, the equations can be graphed on a scale from 0 to 10,000 ppmv. The equations can also be graphed on a log-scale to make the comparisons linear. However, the scale-bias correction factors would not be incorporated if the comparisons are made in this way. Therefore, this type of comparison is not recommended.



Valves-Gas



Valves-Light Liquid

Dotted lines are 90% confidence bounds for the "Refinery" model
Dashed lines are 95% confidence bounds for the SOCMI model

Figure 2-6. Comparison of SOCMI and refinery leak rate correlations.

2.6.3.2 Statistical Comparison of EPA vs. Other Correlations. A more formal approach to comparing leak rate/screening value equations is to use statistical tests to compare the parameters estimated by the equations. The important parameters of the leak rate/screening value equations (developed on a log-scale) are the following:

1) the intercept (Bo);
2) the slope (Bl);
3) the standard error (Se).

Statistical tests for the slope and intercept are also available (Reference 19, page 24-33).

Ninety-five percent confidence intervals for the slope and intercept were developed for each of the SOCMI leak rate/screening value equations (Reference 8, pages 24-25). For example, the slope of the equations for valves in gas service using the OVA was estimated to be 0.693. The 95 percent confidence interval for this slope is given as 0.53 to 0.85. If a slope estimated from a particular SOCMI process unit is within this confidence interval, then the EPA equation provides a reasonable slope for a predictive equation. If the slope estimate is outside the confidence interval for the EPA correlation, the confidence interval for the slope estimated by the unit-specific equation must be evaluated. Reference 19 indicates how to make these evaluations.

A statistical test to compare the standard errors for two equations can be done using an F-test (Reference 20, page 31 or Reference 21, pages 111-116). Since the standard error is the key component of the scale-bias correction factor, this comparison of standard errors will also serve as a comparison of the scale bias correction factors incorporated in the two correlations.

2.6.3.3 Other Statistical Analyses. There are other types of statistical analysis that can be used in the development, evaluation, and comparison of leak rate/screening value equations. A General Linear Models analysis of the leak/rate screening value data (Reference 20, Chapter 2) can be used to develop equations and to test for different leak rate/screening relationships for different groups of data. This approach was used in Reference 14 (pages 51-53) to evaluate differences between the cumene, ethylene, and vinyl acetate units.

2.6.4 Generation of Emission Estimates

The generation of the emission estimate using correlations developed for specific process units makes use of the empirical screening data and the leak rate/screening value correlations. The leak rate/screening value correlations are applied to the screening data to calculate predicted emission rates.

Emission rates are estimated for all emitting sources (including those sources which were bagged) by:

$$\text{Predicted emission rate} = \exp\left[B_0 + B_1 \log(\text{screening concentration})\right] \times (\text{scale bias correction factor})$$

B_0 and B_1 are the coefficient estimates either published by EPA (Appendix D) or developed from a linear regression analysis, if site specific correlations are used. The results presented in arithmetic scale are adjusted to represent mean emission rates using the scale bias correction factor.

The sum of the individual predicted leak rates represents the total mass emission estimate for a given type of source and service being considered. An emission estimate per source can be derived by averaging the total emission estimate over the number of sources in the distribution.

2.6.5 Statistical Considerations for the Predicted Emission Estimate

This section presents formulas for calculating the 95 percent confidence intervals for the predicted emission estimate. For clarity, formulas for calculating the emission estimate per source and total emission estimate are presented also. Definitions for the formulas are presented in the Glossary.

For the Average Emission Rate Per Leaking Source (EE_1):

$$EE_1 \text{ without censoring} = \frac{\sum_{i=1}^{N_1} Y_{1i}}{N_1},$$

with a 95 percent confidence interval of:

$$EE_1 \pm \frac{ts_{y1}}{(N_1)^{1/2}}$$

$$EE_1, \text{ with censoring} = \frac{N_{1a}\,Y_{1a} + N_{1b}Y_{1b}}{N_1},$$

with a 95 percent confidence interval of:

$$EE_1 \pm \frac{t}{N_1}\left(\left[N_{1a}s_{y1a}\right]^2 + \frac{N_{1b}}{n_{1b}} - 1\left[N_{1b}s_{y1b}\right]^2\right)^{1/2}$$

For the Average Emission Rate Per Non-leaking Emitting source (EF_2):

$$EE_2 = \frac{\sum_{i=1}^{N_2} Y_{2i}}{N_2},$$

with a 95 percent confidence interval of:

$$EE_2 \pm \frac{ts_{y2}}{(N_2)^{1/2}}$$

For the Average Emission Rate Per Source (EE):

$$EE = \frac{N_1EE_1 + N_2EE_2}{N_1 + N_2 + N_3},$$

with 95 percent confidence intervals of:

$$EE \pm \frac{t}{N_1 + N_2 + N_3}\left(\left[N_1s_{y1}\right]^2 + \left[N_2s_{y2}\right]^2\right)^{1/2} \text{ without censoring.}$$

Total Emissions + N x EE (use the EE confidence limits above multiplied by N).

3.0 SOURCE SCREENING

This section presents protocols and methodologies for conducting screening of equipment components with a portable organic analyzer. The overall survey procedure is presented to give the perspective of a unit-wide screening plan. In addition, screening protocols are given for the different equipment types. The selection of an appropriate portable monitoring instrument is discussed and a section on data handling is also included.

3.1 SCREENING SURVEY PROCEDURES

For development of a unit-specific emission estimate, the concentration of organic materials at seals, shafts, and other potential leak points must be measured. In preparing to screen all equipment in a unit, all equipment to be included in the emission estimate unit needs to be identified. A listing of equipment types that are potential sources of fugitive emissions is given in Table 3-1.

The first step in the screening survey is to define precisely the process unit boundaries. This is usually quite straightforward, but occasionally multiple units may be built on the same pad and share some common facilities. A process unit can be defined as the smallest set of process equipment which can operate independently and includes all operations necessary to achieve its process objective. The exact basis for the unit definition should be documented. A plot plan of the unit should be obtained and marked with the appropriate boundaries.

The next step is to obtain a simplified flow diagram of the process and note the process streams. The actual screening and data collection can be done most systematically by following each stream. For instance, a logical starting point would be where one of the feed lines enters the process boundary. The screening team would follow that line, screening all sources, until the line terminates at the flanges of a reactor or separation step. Screening would then continue on the outlet side of the reactor or separation equipment. Minor loops like a bypass around a control valve, pump, or heat exchanger should be screened on the initial pass. Larger loops of process equipment, such as parallel passes and processing alternatives, are more

TABLE 3-1. FUGITIVE EMISSION SOURCES

Equipment Types

Pump seals

Compressor seals

Valves

Pressure relief devices

Sampling connections

Flanges, screwed connections, etc.

Open-ended lines

Drains, vents, doors

Agitator seals

Service

Gas/vapor

Light liquid

Heavy liquid

effectively treated as separate streams. If the emission estimate is being generated in support of control strategies for individual chemical compounds, this approach offers the advantage of screening groups of equipment components with roughly the same composition of materials in the line.

Each source should be uniquely identified to indicate that it has been screened. For example, sources can be tagged. Tags can consist of any form of weatherproof and readily visible identification. Alternatively, a process unit can be considered appropriately tagged if the unit has a system of identifying markings with an associated diagram allowing easy location of marked sources. Once all the equipment along the major streams has been screened, the unit should be divided into a grid to search for fittings missed on the initial survey. The unit survey is completed when all sources in the unit have been either screened or identified as a nonhydrocarbon fitting. Leakless equipment and equipment not in VOC (or VHAP) service should not be included in the screening survey. Equipment documented as inaccessible should be included in the survey; such equipment must be screened annually under regulations for fugitive emissions.

Consistent with equipment leaks standards for hazardous air pollutants, unsafe-to-monitor equipment do not need to be included in the survey. Documentation must be provided, however, to substantiate the unsafe nature of such equipment.

3.2 MONITORING INSTRUMENT

A number of portable VOC detection devices are capable of measuring leaks from process units. These devices operate on a variety of principles, the three most common being ionization, infrared absorption, and combustion. Any analyzer can be used provided it meets the specifications and performance criteria set forth in EPA Reference Method 21.[1] Reference Method 21 is included in this document as Appendix A. Any analytical instruments are permitted provided they are shown to measure the organic compounds of interest and the results are related to EPA's data base generated using a flame ionization detector, calibrated to methane. Analytical instruments referenced to compounds other than methane must develop response factors to relate screening values to concentration. This will allow use of many instruments that cannot be calibrated with methane.

3.2.1 Operating Principles and Limitations of Portable VOC Detection Devices

Ionization detectors operate by ionizing the sample and then measuring the charge (number of ions) produced. Two methods of ionization currently used are flame ionization and photoionization.

A standard flame ionization detector (FID) usually measures the total carbon content of the organic vapor sampled. Although carbon monoxide and carbon dioxide do not produce interferences, FID analyzers do react to water vapor, although at a low sensitivity. Furthermore, if water condenses in the sample tube, erratic readings may result. A filter is used to remove particulate matter from the sample. When equipped with options, certain portable FID instruments are capable of measuring total gaseous nonmethane organics or individual organic components. Certain organic compounds containing nitrogen, oxygen, or halogen atoms when sampled with an FID give a reduced response; and some organics may not give any response at all. For this reason, it is necessary to develop response factors for each compound that is to be measured. Response factors are discussed in Section 3.2.2.1.

Photoionization detectors use ultraviolet light (instead of a flame) to ionize organic vapors. As with FID's, the detector response varies with the functional group in the organic compounds. Photoionization detectors have been used to detect leaks in process units used in the synthetic organic chemical manufacturing industry, especially for certain compounds such as formaldehyde that will not give a response on an FID or combustible detector.

Nondispersive infrared (NDIR) instruments operate on the principle of light absorption characteristics of certain gases. NDIR instruments are usually subject to interference because other gases such as water vapor and carbon dioxide may also absorb light at the same wavelength as a compound of interest. These detectors are generally used only for the detection and measurement of single components. For the detection and measurement of single components, the wavelength at which a certain compound absorbs infrared radiation is predetermined and the device is preset for that specific wavelength by using optical filters. For example, if set to a wavelength of 3.4 micrometers, infrared devices can detect and measure petroleum fractions, including gasoline and naphtha.

Combustion analyzers are designed either to measure the thermal conductivity of a gas or to measure the heat produced by combusting the gas. The most common method used in portable VOC detection devices is measuring the heat of combustion. These devices are referred to as hot wire detectors or catalytic oxidizers. Combustion analyzers, like most other detectors, are nonspecific for gas mixtures. In addition, combustion analyzers exhibit reduced response (in some cases, no response) to gases that are not readily combusted, such as formaldehyde and carbon tetrachloride.

3.2.2 Performance Criteria and Evaluation for Portable VOC Detectors

As previously stated, any portable VOC detector may be used as a screening device directly provided it meets the performance criteria specified in Reference Method 21 (see Appendix A). Although this approach has been shown to be applicable to many organics, it cannot be universally applied. Facilities may need to develop an appropriate method for testing inorganic and some organic compounds. A discussion of the performance criteria and detector evaluation procedure is presented below and summarized in Table 3-2.

In addition to the performance criteria, Reference Method 21 also requires that the analyzer meet the following specifications:

- The VOC detector shall respond to those organic compounds being processed (determined by the response factor).
- The analyzer shall be capable of measuring the leak definition specified in the regulation (i.e., 10,000 ppmv or "no detectable limit").
- The scale of the analyzer shall be readable to ±5 percent of the specified leak definition concentration.
- The analyzer shall be equipped with a pump so that a continuous sample is provided at a nominal flow rate of between 0.5 and 3.0 liters per minute.
- The analyzer shall be intrinsically safe for operation in explosive atmospheres.

Also, criteria for the calibration gases to be used are specified. Two or more calibration gases are required for analyzer performance evaluation. One is a zero gas which is air with less than 10 ppmv VOC. The other calibration gases, or reference gases, use reference compounds in air mixtures. The concentration of the reference gas should represent the range

TABLE 3-2. PERFORMANCE CRITERIA FOR PORTABLE VOC DETECTORS[a]

Criteria	Requirement	Time Interval
Instrument response factor	Must be <10 unless correction curve is used.	One time, before detector is put in service.
Instrument response time	Must be ≤30 seconds	One time, before detector is put in service. If modification to sample pumping or flow configuration is made, a new test is required.
Calibration precision	Must be ≤10% of calibration gas value	Before detector is put in service and at 3-month intervals or next use, whichever is later.

[a]Source: Reference Method 21.

of responses measured. For the purpose of developing unit-specific emission estimates, a reference gas for the appropriate range should be used.

3.2.2.1 Response Factor. The sensitivity of an analyzer varies, depending on the composition of the sample and concentration detected. The response factor (RF) helps to quantify the sensitivity for each compound. The response factor is defined by:

$$\text{Response Factor} = \frac{\text{Actual concentration of compound}}{\text{Observed concentration from detector}}$$

It is important to note that the response factor may be used as a guide to selecting an appropriate monitoring device. For example, from the data presented in Appendix B, it can be readily seen that in screening equipment in a process unit containing cumene, an FID can be used (RF = 1.87) directly, with no correction for response factor; while the catalytic oxidation detector cannot (RF has no value). Similarly, from the same data, neither of these devices would be capable of detecting leaks from a source containing carbon tetrachloride if response factor adjustments are not used.

Using response factors as a general guide to analyzer applicability is especially important when dealing with chemical mixtures, since many process streams in industrial plants are composed of mixtures of chemicals. One EPA study concluded that analyzer response factors for a chemical mixture fall between the responses expected for the pure components.[5] Therefore, if desired, an interpolated or weighted average can be used to predict the response for mixtures based on known responses for individual chemicals. If sufficient information on pure components is not available or if desired, the response factor of a mixture for a specific instrument may be determined experimentally in the laboratory. Such results should be well documented. For further information see EPA-600/2-81-110, Response of Portable VOC Analyzers to Chemical Mixtures,[5] and EPA-600/2-8-051, Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds.[4]

Response factors also may be used to correct screening value measurements gathered to estimate emissions when using an emission factor approach (e.g., leak/no-leak approach or three-strata approach). If using leak rate/screening value correlations, however, a standard curve covering the entire range of

screening values measured must be used. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources.[4,5,6] An analyzer's response factor for individual compounds to be measured must be less than 10 at or near the concentrations defining emission factors (e.g., 1,000 and 10,000 ppmv) to be acceptable. The response factor tests are required before placing the analyzer in service, but do not have to be repeated at subsequent intervals.

Response factors can be determined by the following method. First, the analyzer is calibrated using the reference gas. Then, for each organic species that is to be measured, a known standard in air is obtained or prepared. This mixture is then injected into the analyzer and the observed meter reading is recorded. The analyzer is then zeroed by injecting zero air until a stable reading is obtained. The procedure is repeated by alternating between the mixture and zero air until a total of three measurements is obtained. A response factor is calculated for each repetition and then averaged over the three measurements.

Alternately, if response factors have been published for the compounds of interest for the combination of detector and calibration gas desired, the response factor determination is not required, and existing results may be referenced. Results of a study developing response factors of FID (Foxboro OVA-108 and OVA-128) and catalytic oxidation (J. W. Bacharach TLV Sniffer) analyzers are presented in Table B-1 of Appendix B.[4] These response factors can be used when determining if a screening concentration is above or below 10,000 ppmv. The values are for pure organic chemicals only. Table B-2 of Appendix B presents tested compounds that appear unable to achieve an instrument response of 10,000 ppmv at any feasible concentration unless response factors are used.[4] These single response factors are adequate for response factor adjustments when using one of the emission factor approaches for estimating emissions. When applying correlations, however, an accurate correction for the non-linear response of an instrument is needed. Response factors must be evaluated at several concentrations to establish a correction curve for use in translating instrument readings.

3.2.2.2 Response Time. The response time of an analyzer is defined as the time interval from a step change in VOC concentration at the input of a

sampling system, to the time at which 90 percent of the corresponding final value is reached as displayed on the analyzer readout meter. The response time must be equal to or less than 30 seconds. The response time must be determined for the analyzer configuration that will be used during testing, and the response time test is required before placing an analyzer in service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required before further use.

3.2.2.3 Calibration Precision. Calibration precision is the degree of agreement between measurements of the same known value. To ensure that the readings obtained are repeatable, a calibration precision test must be completed before placing the analyzer in service, and at three-month intervals, or at the next use, whichever is later. The calibration precision must be equal to or less than 10 percent of the calibration gas value.

To perform the calibration precision test, a total of three measurements is required for each nonzero concentration. Measurements are made by first introducing zero gas and adjusting the analyzer to zero. The specified calibration gas (reference) is then introduced and the meter reading is recorded. The average algebraic difference between the meter readings and the known value of the calibration gas is then computed. This average difference is then divided by the known calibration value and multiplied by 100 to express the resulting calibration precision as percent.

3.2.2.4 Safety. Portable instruments to detect VOC emissions from equipment leak sources are required to be used in hazardous locations such as petroleum refineries and bulk gasoline terminals. The National Electrical Code requires that instruments to be used in hazardous locations be certified to be explosion-proof, intrinsically safe, or purged.

Hazardous locations are divided into three classes: Class I, Class II, and Class III. Each class is divided into two divisions (Division 1 or 2) according to the probability that a hazardous atmosphere will be present; and also into seven groups depending on the type of hazardous material exposure. Groups A through D are flammable gases or vapors, and Groups E, F, and G apply to combustible or conductive gases. Class I, Division 1, Groups A, B, C, and D locations are those in which hazardous concentrations of flammable gases or

vapors may exist under normal operating conditions. Class I, Division 2, Groups A, B, C, and D locations are those in which hazardous concentrations of flammables may exist only under unlikely conditions of operation.

As of 1982, five manufacturers produced portable VOC detection instruments that are certified to be intrinsically safe. Table 3-3 lists these manufacturers, approved instrument model numbers, instrument certification categories, and performance specifications. Additionally, newer instruments may be available that meet the performance requirements for generating emission estimates.

3.2.3 Monitoring Devices For Difficult Situations

In some cases, a monitoring device may not be available that meets all of the performance specifications of Method 21. For example, there are several cases (e.g., phosgene) where the response factor at 10,000 ppmv is greater than ten (10). The instrument may meet all other requirements, but fails as a Method 21 instrument because it cannot meet the response factor requirement. The instrument can still be used to estimate emissions from equipment leaks, provided the instrument is shown to be sufficiently reliable in providing data that can be related to EPA's data collected using an OVA calibrated to methane.

Several steps must be taken initially to document the viability of a device that fails to meet the Method 21 requirements. First, a laboratory program must be undertaken to demonstrate the response of the monitoring instrument to the compounds being measured. This response must be documented. The second step involves relating the instrument response (i.e., screening value) to actual concentrations, or in other words, developing an instrument response curve. The screening value response curve must be developed for the entire screening value range and documented so that screening values taken in the field can be adjusted to actual concentrations. Third, the testing program should be sufficiently well documented to demonstrate how the instrument will be used in screening equipment. For example, if the response time of the candidate instrument exceeds the Method 21 performance specification, the test plan should reflect added screening time at each potential leak point to be screened. Once this laboratory demonstration has been completed and the screening value correction curve has been established, the screening can begin.

TABLE 3-3. PORTABLE VOC DETECTION INSTRUMENT PERFORMANCE SPECIFICATIONS

Manufacturer	Model No.	Pollutant(s) Detected	Principle of Operation	Range (ppm)	Certification
Bacharach Instrument Co., Santa Clara, California	L	Combustible gases	Catalytic Combustion	0-100% LEL	Intrinsically safe, Class I, Division 1, Groups C and D
	TLV Sniffer	Combustible gases	Catalytic Combustion	0-1,000 and 0-10,000	Intrinsically safe, Class I, Division 1, Groups C and D; and Class I, Division 2, Groups A and B
Foxboro, S. Norwalk, Connecticut	OVA-128	Total hydrocarbons	FID/GC	0-1,000	Intrinsically safe, Class I, Division 1, Groups A, B, C and D
	OVA-108	Total hydrocarbons	FID/GC	0-10,000	Intrinsically safe, Class I, Division 1, Groups A, B, C and D
HNU Systems, Inc. Newton Upper Falls, Massachusetts	PI-101	Chlorinated hydrocarbons, aromatics, aldehydes, ketones, any substance which UV light ionizes	Photo-ionization	0-20, 0-200, 0-2,000	Intrinsically safe, Class I, Division 2, Groups A, B, C and D
Mine Safety Appliances Co., Pittsburgh, Pennsylvania	40	Combustible gases	Catalytic Combustion	0-10% and 0-100% LEL	Intrinsically safe, Class I, Division 1, Group D; and Class I, Division 2, Groups A, B, and C
Survey and Analysis, Inc., Northboro, Massachusetts	On Mark Model 5	Combustible gases and vapors	Thermal Conductivity	0-5 and 0-100% LEL	Intrinsically safe, Class I, Division 1, Groups A, B, C and D

3.3 SCREENING PROCEDURES

3.3.1 Calibration Procedures

Pretest procedures to be followed include calibration of the monitoring instrument. The VOC analyzer should be assembled and started up according to the manufacturer's instructions. After the appropriate warm-up period and zero internal calibration procedure, the calibration gas is introduced into the sample probe. The instrument meter readout is then adjusted to correspond to the calibration gas value. If the meter readout cannot be adjusted to the proper value, a malfunction of the instrument is indicated and corrective measures should be taken before use.

3.3.2 Procedure for Screening Equipment

The mechanics of the screening operation outlined in Reference Method 21 are summarized in the following discussion. The probe inlet is placed at the surface of the leak interface where leakage could occur. (The leak interface is the boundary between the process fluid and the atmosphere.) Care must be taken to ensure that the probe is held perpendicular, not tangential, to the leak interface. Otherwise, inaccurate readings will result. The probe must then be moved along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly move the probe along the interface where leakage is indicated until the maximum meter reading is obtained. The probe inlet should be left at this maximum reading location for approximately two times the instrument response time. The maximum reading is recorded as the screening value.

The instrument measurement may exceed the scale of the instrument. For example, the reading may exceed 10,000 ppmv when using an OVA analyzer. For the purposes of generating an emission estimate, these higher readings also must be recorded. A dilution probe should be employed to allow measurement of concentrations greater than the instrument's normal range. The OVA can be equipped with a dilution probe that permits measurement of concentrations up to 100,000 ppmv. It is important to note that extending the measurement range also necessitates the calibration of the instrument to the higher concentrations.

Care should be taken to avoid fouling of the probe with grease, dust, or even liquids. A short piece of Teflon tubing can be used as a probe tip

extender and snipped off as the tip fouls. In areas with a noticeable particulate loading, this tubing can be packed with untreated fiberglass to act as a filter. (Note that the instrument must also be calibrated with this filter in place). If a surface to be screened is obviously dirty, hold the probe tip just over the surface to avoid scooping up contaminants. Some fouling is unavoidable, so it is recommended that the probe tip sintered steel filter be cleaned at least daily and the side-pack filter on a weekly basis. Normally, these filters can be cleaned by just rapping them lightly on a table top, but if the deposits are wet and caked on, washing with an aqueous solution of soap and alcohol is recommended. This can also be used to wash the probe and transfer line periodically. Care should be taken to blow the equipment dry before reuse.

This general procedure can be used to screen equipment such as valves, flanges, pumps and compressors, pressure relief devices, and other potential sources of VOC leakage such as process drains and open-ended lines or valves.

For valves, the most common source of leaks is at the seal between the stem and housing. To screen this source, the probe is placed where the stem exits the packing gland. The probe is moved around the stem circumference. The maximum reading is recorded as the screening value. Also, the probe is placed at the packing gland take-up flange seat and the probe is moved along the periphery. In addition, valve housings of multipart assemblies should be screened at the surface of all points where leaks could occur. Figures 3-1 through 3-5 illustrate screening points for several different types of valves.

For flanges, the probe is placed at the outer edge of the flange-gasket interface and the circumference of the flange is sampled. For screwed flanges, the threaded connection interface must also be screened. Other types of nonpermanent joints, such as threaded connections, are sampled with a similar traverse.

Pumps and compressors are screened with a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface where the shaft exits the housing. If the source is a rotating shaft, the probe inlet is positioned within 1 cm of the shaft-seal interface. If the housing configuration prevents a complete traverse of the shaft periphery, all accessible portions must be sampled. All other joints on the pump or

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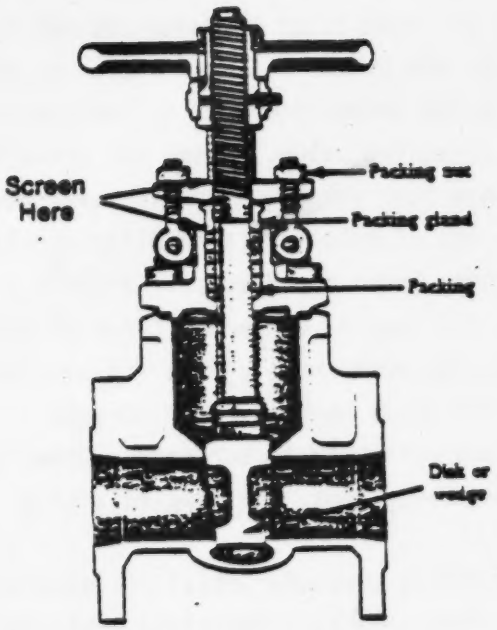

Figure 3-1a. Rising stem type.

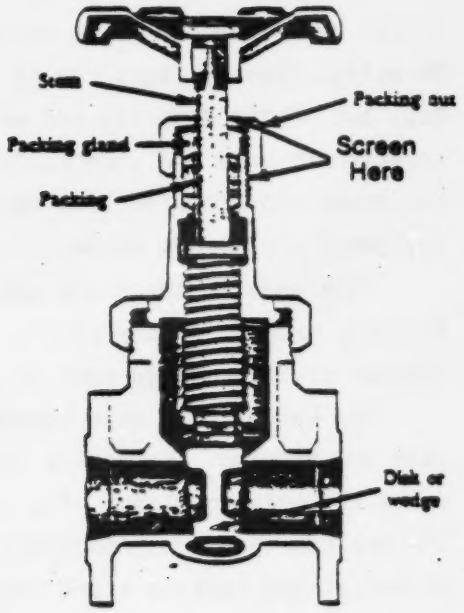

Figure 3-1b. Non-rising stem type.

Figure 3-1. Gate valves.

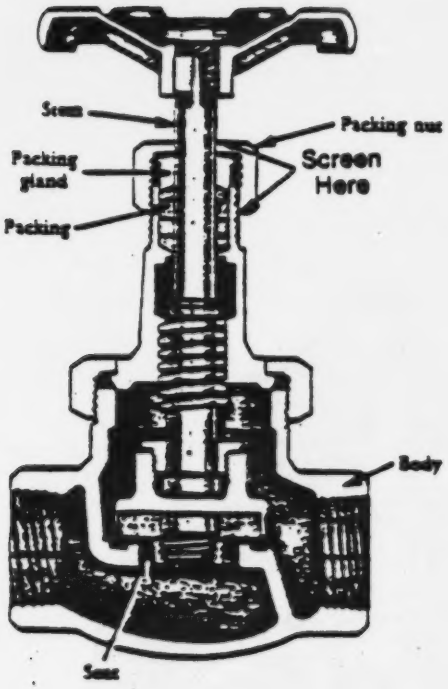

Figure 3-2a. Manual Globe Valve

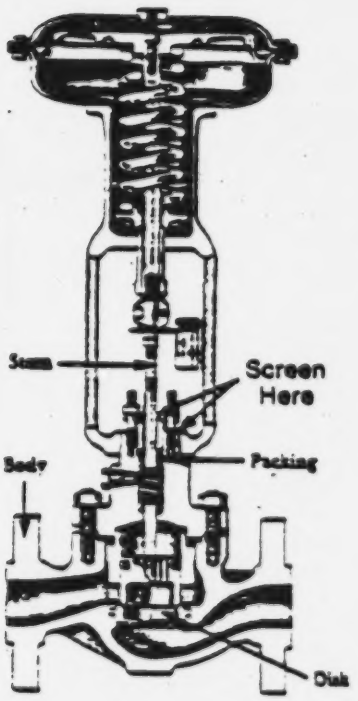

Figure 3-2b. Globe type control valve

Figure 3-2. Globe valves.

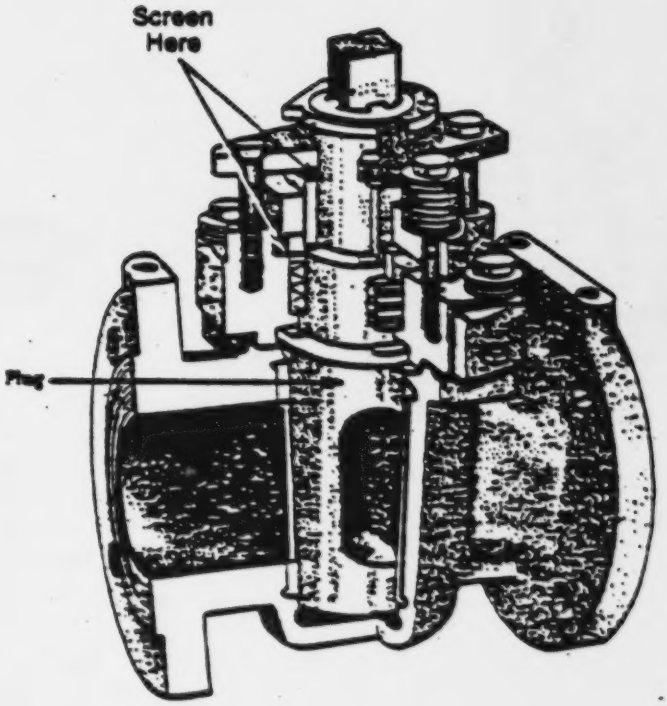

Figure 3-3. Lubricated plug valve.

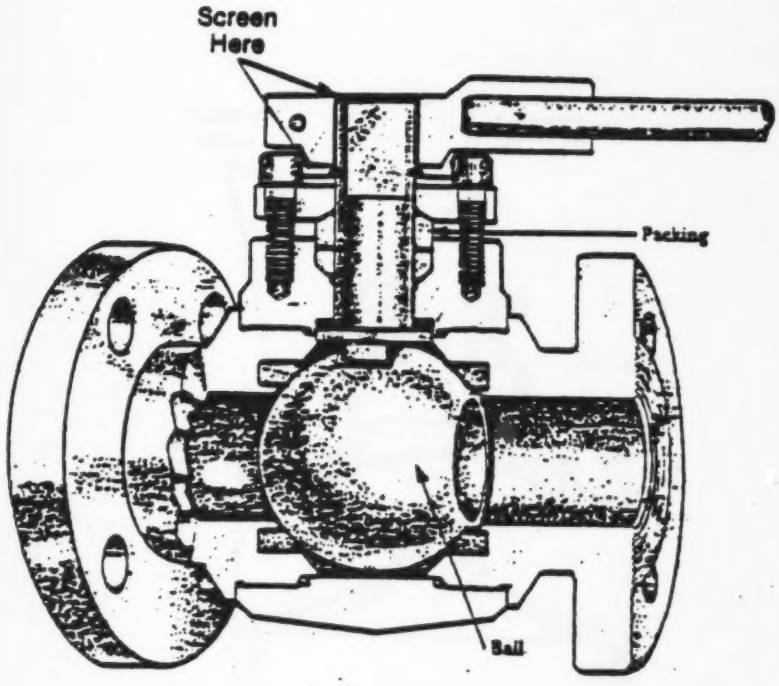

Figure 3-4a. Ball valve.

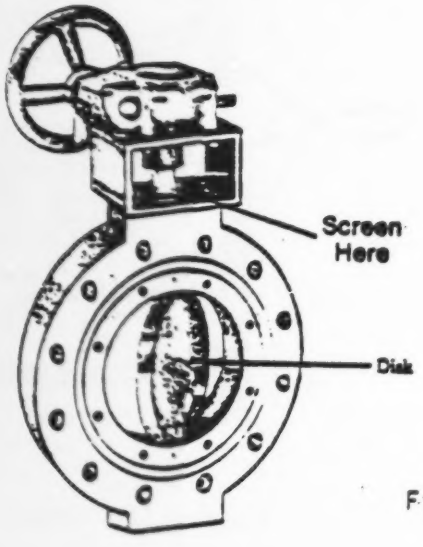

Figure 3-4b. Butterfly valve.

Figure 3-4.

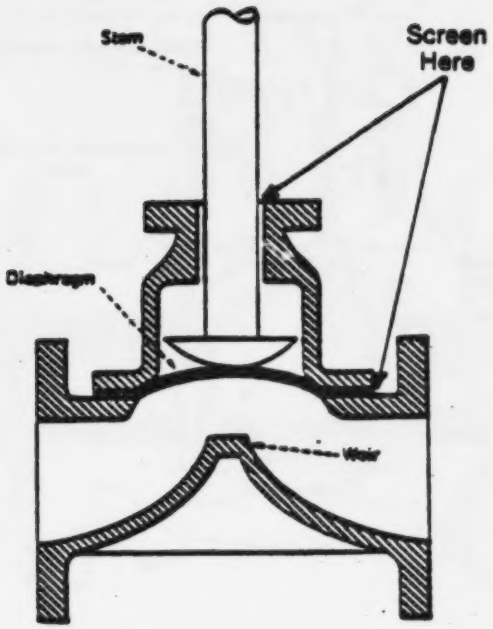

Figure 3-5a. Weir type diaphragm valve.

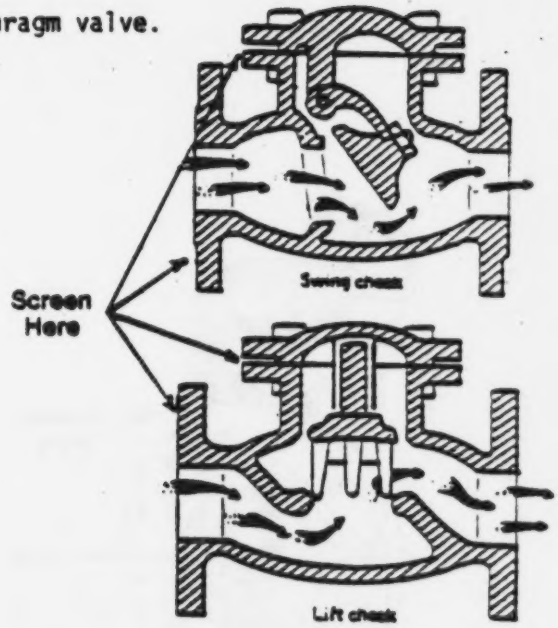

Figure 3-5b. Check valves.

Figure 3-5.

compressor housing where leakage could occur should also be sampled. Figure 3-6 illustrates screening points for two types of centrifugal pumps. Agitator seals should be screened in a similar manner.

The configuration of most pressure relief devices prevents sampling at the sealing seat. Because of their design and function, pressure relief devices must be approached with extreme caution. These devices should not be approached during periods of process upsets, or other times when the device is likely to activate. Similarly, care must be used in screening pressure relief devices to avoid interfering with the working parts of the device (e.g., the seal disk, the spring, etc.) For those devices equipped with an enclosed extension, or horn, the probe inlet is placed at approximately the center of the exhaust area to the atmosphere. Again, only the probe should be placed in the horn; personnel conducting the screening should not place hands, arms, or any parts of the body into the horn. Figure 3-7 illustrates the screening points for a spring-loaded relief valve.

Fugitive leaks from most other sources such as process drains, open-ended lines or valves, and seal system degassing vents and accumulator vents, are emitted through a regularly shaped opening. If that opening is very small (as in sampling lines of less than one inch diameter), a single reading in the center is sufficient. For larger openings (like a six inch drain mouth), it is necessary to traverse the perimeter of the opening. The concentration at the center must also be read. For even larger sources (like a wash-up drain grate), a grid of readings should be taken on about six inch centers. For access door seals, the probe inlet is placed at the surface of the door seal for the peripheral traverse. For all of these types of equipment, it is the maximum value that is recorded as the screening concentration.

3.4 DATA HANDLING

To handle the screening data uniformly, it is recommended that data be recorded on prepared data sheets. The data collected should include the following:

1. Date.
2. Hydrocarbon detector type.
3. Source identification. (If permanent ID's are not in place, assign ID's consecutively as each source is screened. The first source screened is assigned ID1, the second source screened, ID2, and so on.)

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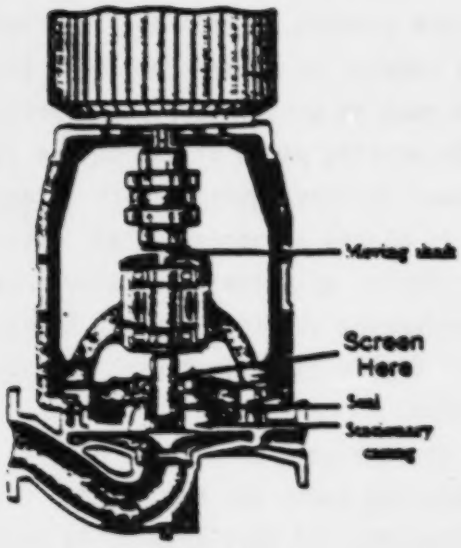

Figure 3-6a. Vertical centrifugal pump.

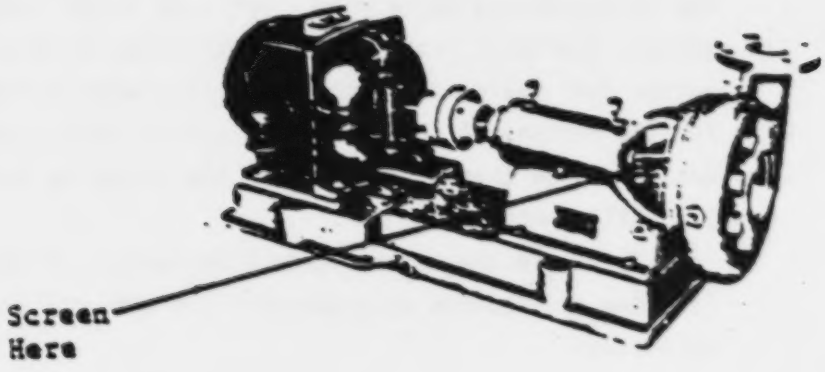

Figure 3-6b. Horizontal centrifugal pump.

Figure 3-6.

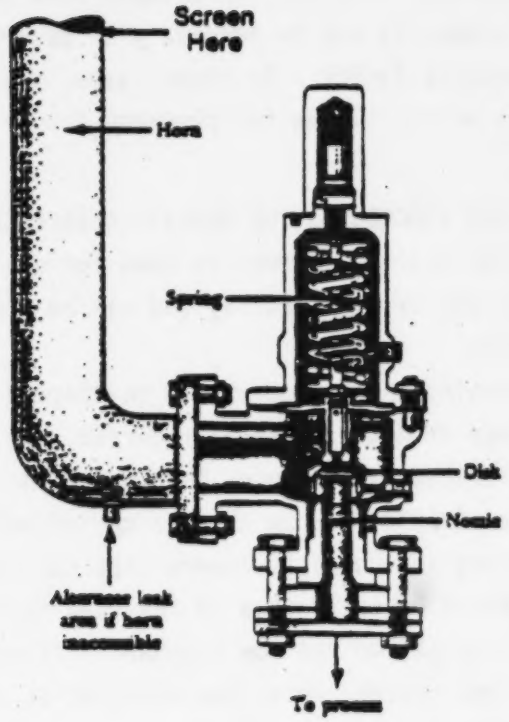

Figure 3-7. Spring loaded relief valve.

4. Screening value recorded in ppmv.

5. Source type (i.e., type of valve, pump, compressor, flange, etc.)

6. Service. For example, gas, light liquid, and heavy liquid. Liquids are classified based on their most volatile component present at 20 weight percent or more. If the components have a total vapor pressure equal to or greater than 0.04 psi at 20°C, the material (containing greater than or equal to 20 percent VOC) is classified as a light liquid; if not, it is classified as a heavy liquid. Classification is based upon the actual process conditions, not ambient conditions.

7. Comments. If any explanation is required, it should be noted in a "comments" section. An example data sheet is given in Table 3-4.

In some cases, it may be necessary or desirable to adjust the screening values for response factor. In these cases, the data sheet should be designed to accommodate extra columns for response factor and corrected screening values.

3.5 CALIBRATION PROCEDURES FOR QUALITY ASSURANCE

Calibration procedures must be used for quality control to ensure the collected data are of high quality and can be compared to the data already gathered by EPA.

Each screening instrument should be checked for calibration before each use and readings from these checks recorded. As an example, instruments should be calibrated each morning before use and before use in the afternoon. The calibration should also be checked periodically (such as during breaks in the daily testing schedule) to ensure that calibration has not drifted. The instruments should be calibrated if the reading is off by more than $\pm$5% on the high standard, or $\pm$20 on the low standard. If more than one instrument is being used at one process unit, the calibration readings for all instruments must be recorded.

TABLE 3-4. EXAMPLE DATA SHEET

Date	Hydrocarbon Detector Type	Source ID	Screening Value (ppmv)	Process Unit	Service	Primary Material	Comments

SECTION 4.0
MASS EMISSIONS SAMPLING

The process of measuring organic concentrations at potential leak points of equipment when combined with the EPA's leaking and non-leaking emission factors gives a good estimate of the leak rate from a process unit. More rigorous procedures may be used to determine the mass emission rate more accurately. Measuring mass emission rates requires source enclosure combined with sampling of the gas in the enclosure. The dilution or vacuum method is the preferred technique for sampling the emissions from sources that can be enclosed. An alternate sampling technique is the blow-through method which is usually used for sources with very large leak rates (in excess of the vacuum pump capacity). An important step in either of these methods, however, is source enclosure, a procedure called bagging.

4.1 VACUUM METHOD

In the past, the method preferred for sampling leaks from baggable sources has been the dilution or vacuum method. The sampling train used in this method is shown in Figure 4-1.

The train can be mounted on a portable cart, which can be easily moved around the process unit from source to source. -The major equipment items in the sampling train are the vacuum pump used to draw air through the system, and the dry gas meter used to measure the flow rate of gas through the train. In previous studies that EPA conducted, a 4.8 CFM Teflon-ring piston type vacuum pump equipped with a 3/4-horsepower air-driven motor was used. Low pressure air (~100 psig) is available at or near most process units. An example of a suitable dry gas meter is a Rockwell Model 1755 Test Gas Meter with a Number 83 Test Index.[12] Other equipment that EPA used in the train includes Whitey valves, copper and stainless steel tubing, Teflon tubing, 100 cc glass airtight syringe, thermometers, mercury and water manometers, a cold trap, and an air-driven diaphragm sampling pump.

The leak source is shown as a valve in Figure 4-1. However, the same sampling train can be used for all equipment to be sampled using the vacuum technique. As described in Section 4.3, the size and shape of the enclosure (tent) around the potential leak point is adjusted to fit the particular shape

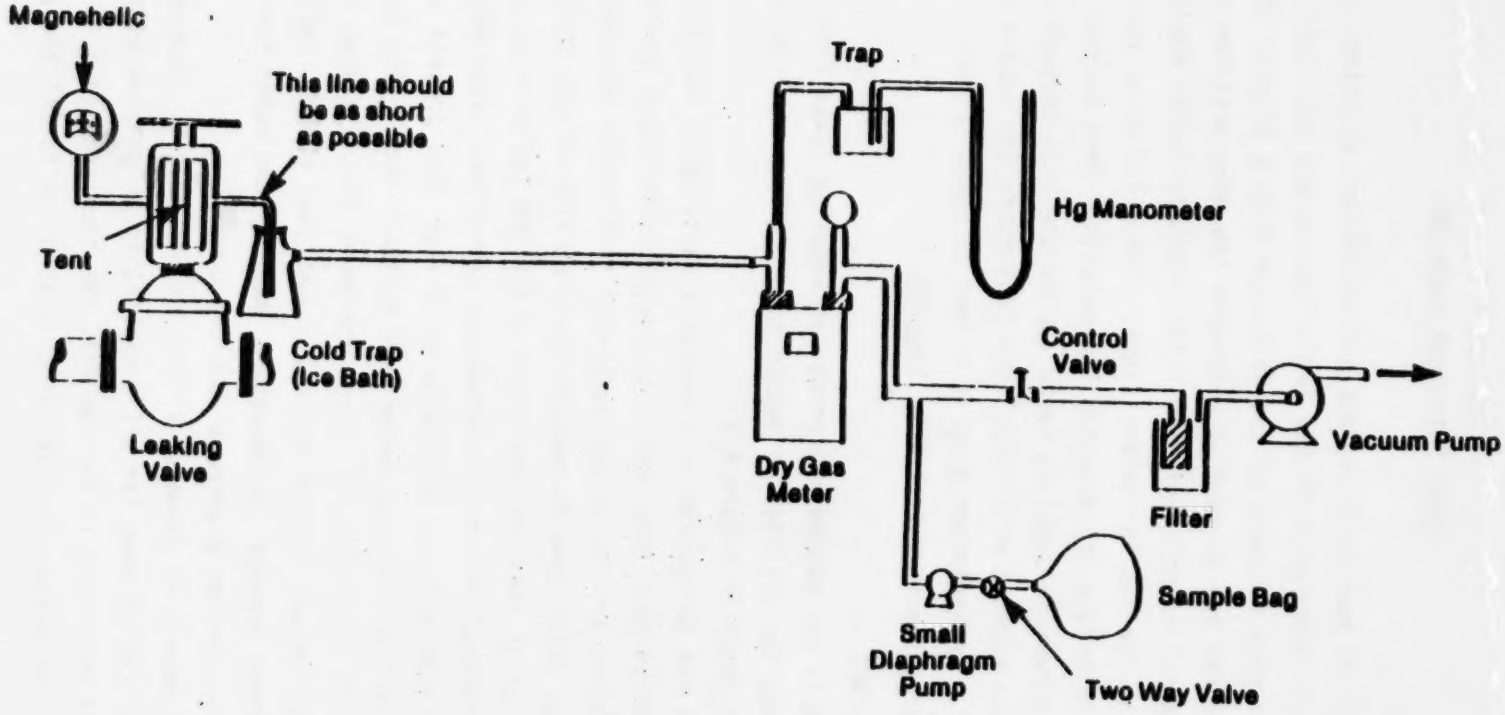

Figure 4-1. Sampling train for baggable sources of hydrocarbon emissions using a diaphragm.

and operating condition of the equipment. When the full sampling train is connected, the vacuum pump is able to maintain a maximum flow rate of approximately 2.5 cubic feet per minute (0.001 cubic meters per second).

The tent is connected by means of a bulkhead fitting and Teflon tubing to the sampling train. A separate line is connected from the tent to a magnahelic to allow continuous monitoring of the pressure inside of the tent. If a significant vacuum exists inside the tent when air is being pulled through, a hole is made in the opposite side of the tent from the outlet to the sampling train. This allows air to enter the tent more easily and thus reduces the vacuum in the enclosure. In practice, it has been found that only a very slight vacuum (0.1 inches H_2O) is present in the tent during most of the sampling, even in the absence of a hole through the tent wall. Sufficient air enters around the seals to prevent the development of a significant vacuum in the tent. Sample bags are used to collect gas samples and transport them to the laboratory for analysis. As with the tent material, sample bags must be constructed of material that is impermeable to hydrocarbons so that the process components are contained within the sample bag. Mylar plastic, Teflon, and Tedlar are materials well suited to this function. A typical sample bag is shown in Figure 4-2.

A cold trap is placed in the system to condense water and heavy organics, thus preventing condensation in downstream lines and equipment. The cold trap can be simply a 500 ml flask in an ice bath placed as close as possible to the tent. While not always necessary, this ice bath cold trap is very effective in preventing condensation in the remainder of the sampling train and in the gas sample bag. Any organic condensate that collects in the cold trap must be measured for later use in calculating total leak rates. On some streams the use of a cold trap is critical.

The flow rate through the system can be varied by throttling the flow with a control valve immediately upstream of the vacuum pump. As the flow rate is decreased, the concentration of hydrocarbon increases in the gas flowing through the sampling system. This allows considerable flexibility in avoiding operations with an explosive mixture of hydrocarbon in the air. If an explosive mixture is present, the blow-through method should be used.

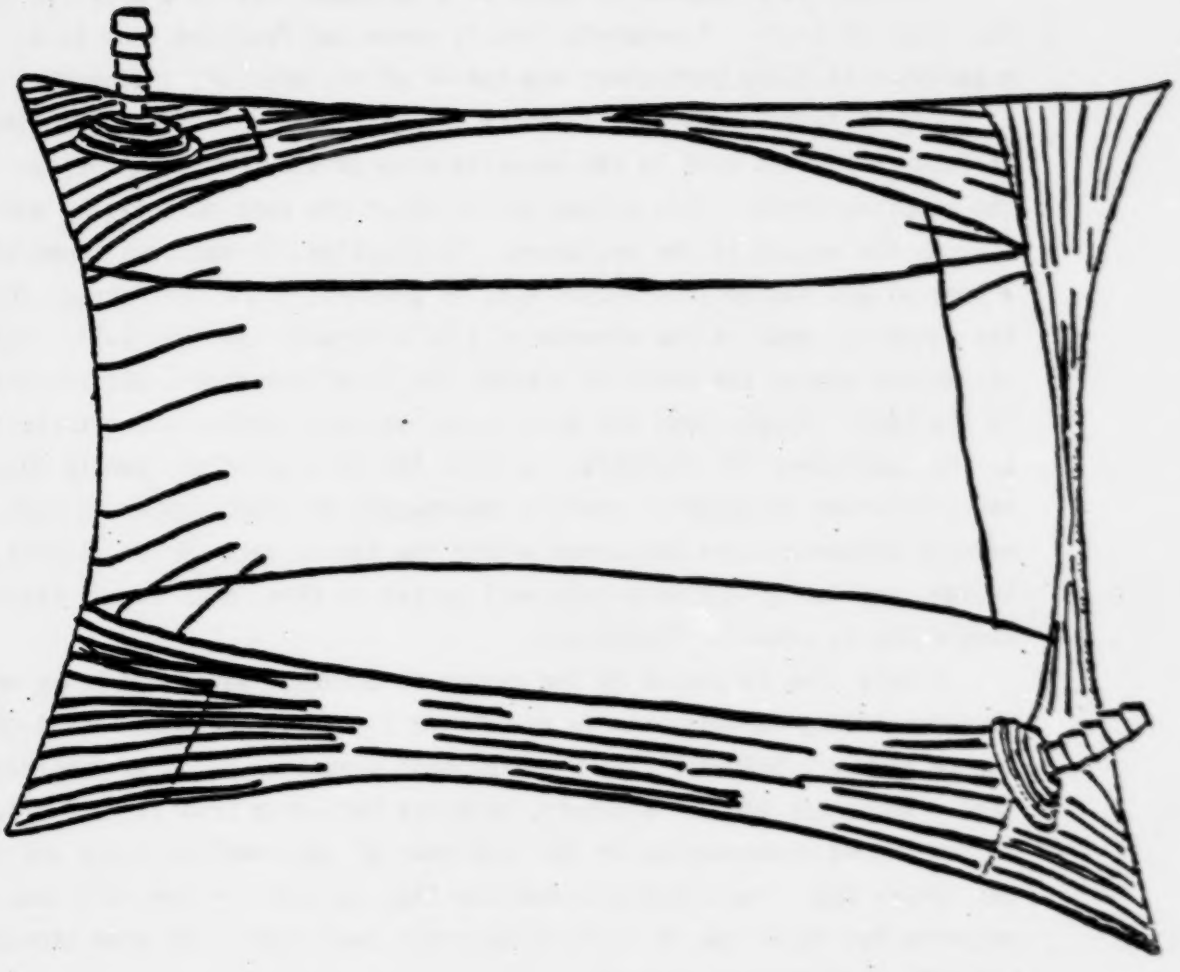

Figure 4-2. Mylar plastic sample bag.

In summary, the vacuum sampling procedure consists of the following steps:

- Obtain and record a screening value with the portable hydrocarbon detector,
- Enclose the source in a tight shroud,
- Connect the tent to the sampling train,
- Immerse the cold trap in an ice bath,
- Note the initial reading of the dry gas meter,
- Start the vacuum pump and a stopwatch simultaneously,
- Record the temperature and pressure at the dry gas meter,
- Observe the VOC concentration at the vacuum pump exhaust with the hydrocarbon detector,
- Record the temperature, pressure, dry gas meter reading, outlet VOC concentration and elapsed time every 2 to 5 minutes,
- Fill a gas sample bag from the discharge of the Teflon-lined diaphragm pump when the outlet VOC concentration stabilizes (i.e., the system is at equilibrium),
- Fill another bag with ambient air near the tent area to detect the background VOC concentration,*
- Take a final set of readings and stop the vacuum pump,
- Remove, seal, and transport the cold trap is to the laboratory along with the two bag samples and the data sheet,
- Remove the tent,
- Rescreen the source with the portable hydrocarbon detector and record.

All of the above data and any pertinent comments should be recorded in a permanent laboratory notebook.

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*This bag sample may be omitted in favor of the hydrocarbon detector reading if the background VOC concentration is less than 5 percent of the lower limit of the screening range (i.e., <50 ppm for the 1,000 to 10,000 ppm class). When bagging a "zero" screening value component, it is extremely important to take a background bag. Data obtained without a background bag will bias emission factors on the high side unless this correction is made.

4.2 BLOW-THROUGH METHOD[a]

Blow-through refers to blowing nitrogen through a flexible tent to create a constant VOC concentration inside the tent. Nitrogen is metered into the tent through 1 or 2 polyvinyl chloride tubes. The temperature and oxygen concentrations are measured inside the tent with a platinum-RTD thermocouple and an oxygen/combustible gas monitor. The flow of nitrogen is monitored in a gas rotameter calibrated to nitrogen. The nitrogen passes though activated charcoal and drierite to remove any organics and moisture. The pressure in the tent never exceeds 1 psig. Figure 4-3 illustrates the equipment required for the blow-through method.

At least two OVA (Foxboro 108 Organic Vapor Analyzer) measurements are made inside the tent, each measurement at two or more differing nitrogen flow rates to increase accuracy. [The OVA must be attached to a dilution probe and calibrated to nitrogen-diluted gases to allow its use in the nitrogen atmosphere in the tent.] The OVA readings are converted to emission rates of VOC via response factors for the OVA; the calculation is shown in Table 4-1. Alternatively, gas samples from the tent can be collected with a portable sampling pump and transported to a lab for chemical speciation and concentration measurement. The calculation in Table 4-1 is also applicable for concentrations measured in this manner (except that the response factor is set equal to 1).

The oxygen concentration is also measured to determine the total gas flow rate through the tent. However, oxygen concentration is also used to rate the quality of the tent, and except for a few extremely difficult situations, VOC concentrations are not measured until the oxygen concentration in the tent is reduced below 5%.

Air can replace nitrogen as a dilution gas if the hydrocarbon concentration is not expected to be high enough to cause an explosive atmosphere inside the tent. However, calculations based on air tent data must assume a nominal tent leakage rate, i.e., extra flow through the tent due to air entering the tent that is not metered through the tubing.

Safety has been a key factor in the development of this procedure. Over 400 valves have been tented with this technique without incident. Nitrogen is

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[a]Text adapted from Chemical Manufacturers Association, Guidance for Estimating Fugitive Emissions, July, 1987.

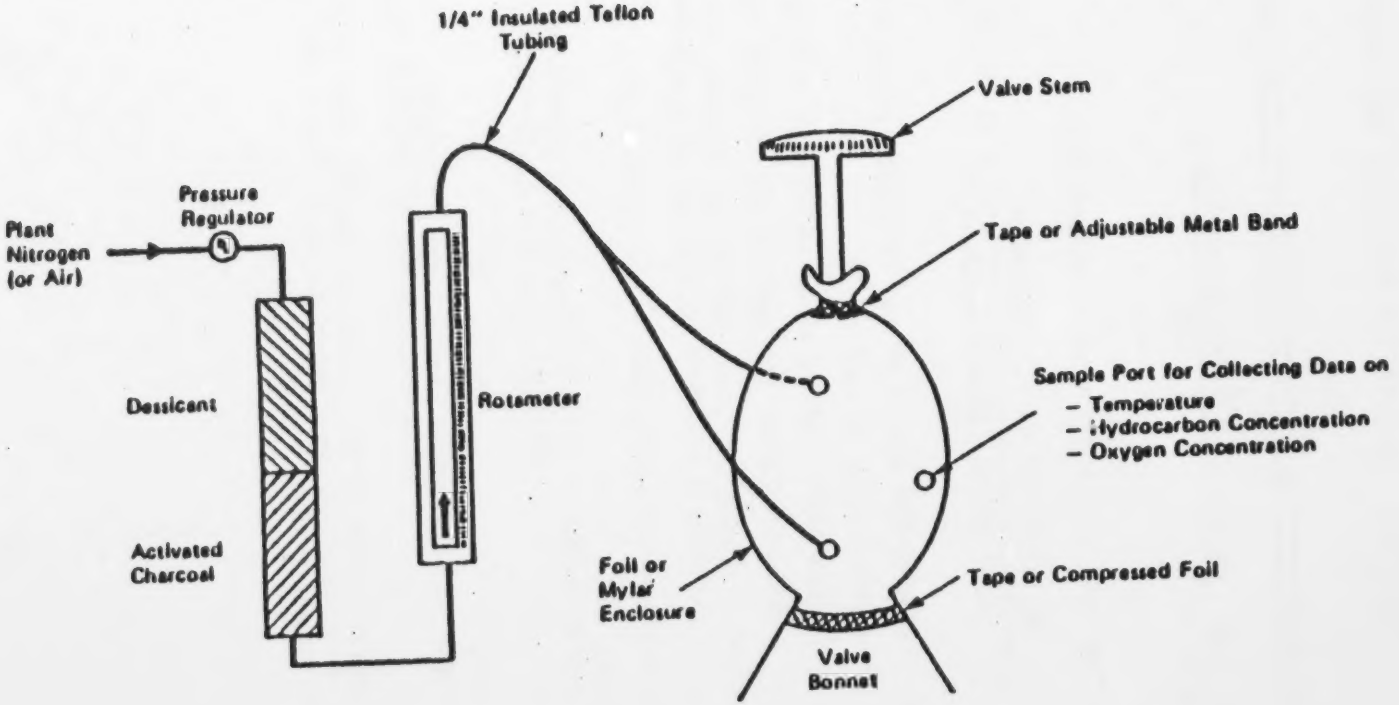

Figure 4-3. Equipment required for the blow-through sampling technique.

TABLE 4-1. CALCULATION PROCEDURES FOR TENTED LEAK RATE

$$\text{Tent rate (lb/hr)} = \frac{4.836 \times 10^{-5}\,(Q)(MW)(OVA)(RF)}{T + 460}$$

where

Q = flow rate into tent in cubic meters/hour

$$= \frac{N_2 \text{ flow rate in liters/minute}}{1 - \left(\frac{\text{tent oxygen concentration in \%}}{21}\right)} \left[0.06 \frac{m^3\text{-minute}}{\text{liter-hour}}\right]$$

MW* = molecular weight of gas in pounds/pound-mole

T = temperature in tent in ^{o}F

OVA = instrument reading minus background reading, in vppm

RF** = response factor for leaking gas relative to calibration gas

4.836×10^{-5} = a conversion factor taking into account the gas constant and assuming a pressure in the tent of 1 atmosphere

*For mixtures:
gas molecular weight = (mole fraction-gas 1)(molecular weight-gas1) + (mole fraction-gas 2)(molecular weight-gas 2) + ...

**For mixtures:
gas response factor = (mole fraction-gas 1)(response factor-gas 1) + (mole fraction-gas 2)(response factor-gas 2) + ...

where response factor is calculated at the OVA concentration. For liquid mixtures, a detailed analysis based on vapor-liquid equilibrium must be done to use OVA concentrations.

used as a dilution gas instead of air to prevent an explosive atmosphere within the tent. All of the instruments used are battery-operated and approved for Class I, Division I use. In summary, the blow-through method consists of the following steps:

- Interview the unit operator to determine the composition of the material in the designated equipment component (in weight or volume %), and the operating conditions of the component.
- Screen the component by placing a Tygon nozzle on the end of the Foxboro/Century OVA (Organic Vapor Analyzer), holding the end of the nozzle within 1 centimeter of the leak interface, and recording the highest concentration seen on the OVA readout.
- Cut a tent from appropriate material (see section 4.3 - Source Enclosure) that will easily fit over the equipment component.
- Connect tubing from the nearest low pressure nitrogen station to a rotameter stand, which includes a regulator, dessicant, activated charcoal, and a rotameter in series.
- Run tubing from the rotameter outlet to a "Y" that splits the nitrogen flow into two pieces of tubing. Insert the tubes into openings located on either side of the tent.
- Turn on nitrogen at the utilities station and regulate it at the rotameter to approximately 40 liters/minute.
- After the nitrogen is flowing, wrap aluminum foil around those parts of the equipment component where air could enter the tent-enclosed volume.
- Use duct tape, wire, and/or rope to secure the tent to the component.
- Put a third hole in the tent roughly equidistant from the two nitrogen-fed holes.
- Measure the oxygen concentration in the tent by inserting the lead from an O_2 meter into the third hole. Adjust the tent (add additional tape, foil, rope, etc.) until the O_2 concentration is less than 5%.
- Measure the temperature in the tent with a platinum-RTD thermocouple.
- Calibrate the OVA to methane or hexane at a known concentration in nitrogen using the OVA dilution probe. Remember to correct for the dilution before inserting the OVA concentration reading into the calculation in Table 4-1.

- Check the VOC concentration at several points in the tent with the OVA to insure that the tent contents are at steady state.

- Measure the hydrocarbon VOC concentration in the tent with the OVA at three different nitrogen flow rates. Typically the flow rates will be 40, 30 and 20 liters/minute if there is no OVA response at the higher rates (i.e., the mass leak rate from the component is very low). After each adjustment of the nitrogen flow, check the O_2 concentration to ensure it stays below 5%. Alternatively, collect samples in Tedlar or aluminized sample bags by drawing sample out of the bag with a portable sampling pump.

- Remove the tent and any plugs from the component and collect any condensate on the inside of the tent in a plastic graduated cylinder. Record the amount collected and the elapsed time the tent was on the component.

- If there is liquid dripping from the component, collect the drips for a timed period which produces enough collected material for accurate volume measurement. Record the amount in the report, but do not add it to the vapor leak rate.

4.3 SOURCE ENCLOSURE

To measure the leak rate from any given fitting accurately, it is necessary to isolate that fitting from the ambient air. This is accomplished by an enclosure (or tent) formed around the leak source. Appropriate tent material must be selected, so that the substances found in the process fluid are contained within the tent. For example, because polyethylene is permeable to hydrocarbons, it is an inappropriate tent material. By comparison, Mylar plastic (polyethylene terephthalate) is well suited to this function as it does not absorb significant amounts of hydrocarbons, it is very tough, and it has a high melting point (250°C). Other suitable materials are Tedlar (PVF film) and Teflon (fluorocarbon resin). For convenience, Mylar will be used as an example of tent material in the following discussions. The thickness of the tent material can range from 1.5 to 15 mil depending on the type of equipment being bagged. A typical tent is shown in Figure 4-4. The enclosures should be kept as small as practical. This has several beneficial effects:

- the time required to reach equilibrium is kept to a minimum,
- the time required to construct the enclosure is minimized,
- a more effective seal results from the reduced seal area, and

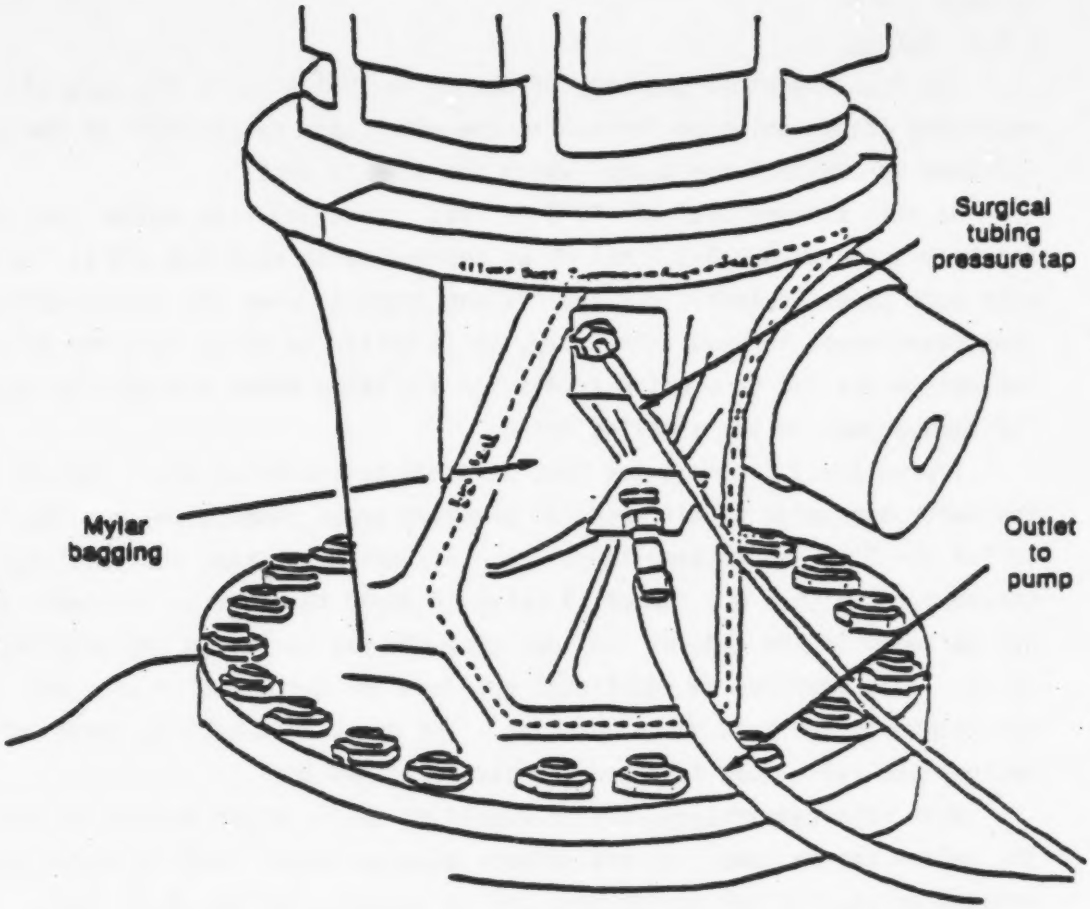

Figure 4-4. Tent construction around the seal area of a vertical pump.

- condensation of heavy hydrocarbons inside the enclosure is minimized or prevented due to reduced residence time and decreased surface area available for heat transfer.

Tent construction for individual sources is discussed in the sections 4.3.1 through 4.3.5.

4.3.1 Valves

The most important property of the valve that affects the type of enclosure (tent) selected for use is the metal skin temperature of the area enclosed by the tent and around which the seal is made.

At skin temperatures of 400°F or less, the valve stem and/or stem support can be wrapped with 1.5-2.0 mil Mylar and sealed at each end and at the seam with duct tape. A leak-tight seal is not required when the vacuum method of leak measurement is used. Actually, it is better to allow for some areas of incomplete sealing to provide access for air being drawn through the tent by the vacuum pump in the sampling train.

Two bulkhead fittings are then attached to the Mylar tent. One is for the water manometer or differential pressure gauge connection, and the other is for the line to the sampling train. If, after starting the sampling, a vacuum greater than 0.1 inches of water is found to exist in the tent, a hole can be added on the side of the tent opposite the outlet to the sampling train. This provides an additional entrance for the dilution air, and reduces the vacuum in the tent while sampling. The Mylar tent must be constructed to enclose the valve stem seal and the packing gland seal.

When skin temperatures are in excess of 400°F, other methods of tenting the valves can be used. In one method, adjusted metal bands or wires are wrapped around all hot points that are in contact with the Mylar tent material. Seals are then made against the insulation using duct tape or adjustable metal bands of stainless steel.

At extremely high temperatures, metal foil can be wrapped around the valve leak area. In a previous study, seals were made using adjustable metal bands.[11] At points where the shape of the equipment prevented a satisfactory seal with metal bands, the foil was crimped to make a seal. It was necessary, in some of these instances, to use a relatively high capacity vacuum pump to insure a constant inflow of air through all seal areas.

Mixed-phase valve leaks are enclosed with the same type of tent described above. The rate of leakage of liquid is measured by collecting it over a measured length of time. A low point is formed in the tent to collect the liquid so its volume can be measured and converted to a mass rate. The total mass leak rate can then be estimated by adding the liquid mass leak rate to the gas mass leak rate.

4.3.2 Pumps and Agitators

As with valves, the property of most concern when preparing to sample a pump or agitator is the metal skin temperature at areas or points that are in contact with the tent material.

At skin temperatures below 400°F, Mylar plastic and duct tape are satisfactory materials for constructing a tent around a pump or agitator seal. The vast majority of centrifugal pumps in VOC service have a housing or support that connects the pump drive (or bearing housing) to the pump itself. The two supports normally enclose about half of the area between the pump and drive motor, leaving open areas on the sides. It is usually a relatively simple matter to cut panels to fit these remaining open areas. In a previous study, the panels were cut from 14 mil Mylar.[11] Bulkhead fittings for the outlets to the water manometer and sampling train are placed through one Mylar panel and sealed. An opening (hole, bulkhead fitting) is made in the opposing panel, if necessary, to allow easier flow of dilution air into the enclosure around the seal.

In many horizontal pumps, there is a line from the bottom of the lower metal support to a drain. This line serves as a drain for coolant, sealant, and/or process liquid leaking from the pump seal. This line (and all other lines from the enclosure) should be sealed off to avoid drawing air and hydrocarbon vapors from the drain back up to the sealed enclosures. If there is no liquid flowing through this drain line, it can be plugged off. If liquid is going to the drain, a short length of hose or tubing can be attached to the end of the drain line and looped upward to form an effective liquid seal.

In the cases where supports are absent or quite narrow, a cylindrical enclosure around the seal can be made so that it extends from the pump housing to the motor or bearing support. This enclosure can be made of 14 mil Mylar, since this thickness provides considerable strength and rigidity.

Reciprocating pumps present a somewhat more difficult tenting problem. If supports are present, the same type of two-panel Mylar tent can be constructed as that for centrifugal pumps. In many instances, however, sufficiently large supports are not provided, or the distance between pump and driver is relatively long. In these cases, a cylindrical enclosure similar to that used for centrifugal pumps can be constructed. If it is impractical to extend the enclosure all the way from the pump seal to the pump driver, a seal can be made around the reciprocating shaft. This can usually be best made by using heavy aluminum foil and crimping it to fit closely around the shaft. The foil is attached to the Mylar plastic of the enclosure and sealed with duct tape.

If the temperature is too high or the potential points of contact are too numerous to insulate, an enclosure made of aluminum foil can be constructed. This enclosure is sealed around the pump and bearing housing using silicone fabric insulating tape, adjustable metal bands, or wire.

In cases where liquid and vapors are leaking from a pump, the enclosures described above for valves can be used. The outlet from the tent to the sampling train is placed at the top of the enclosure and as far away from spraying leaks as practical. Thus, entrainment of the liquid into the sampling train (and cold trap) is avoided. The rate of leakage of liquid is measured by collecting it over a measured length of time. A low point is formed in the tent to collect the liquid so its volume can be measured and converted to a mass rate. The total mass leak rate can then be estimated by adding the liquid mass leak rate to the gas mass leak rate.

4.3.3 Compressors

In general, the same types of tents that are suitable for pumps can be directly applied to compressors. The construction and application of these enclosures have been described in the preceding discussions of pump sampling and will not be repeated in this section.

Compressors generally handle light gases, and in many cases, the seals are enclosed. The seal enclosures are vented to the atmosphere at a high-point vent or may be vented to the blowdown/flare system.

If the seals are vented to a high-point vent, this vent line can be sampled. A Mylar bag can be constructed and sealed around the outlet of the

vent and connected to the sampling train. The leak rate from the vented compressor seals is then measured using the normal flow-through method.

If the high-point vents are inaccessible, the vent lines from the compressor seal enclosures can be disconnected at some convenient point between the compressor and the normal vent exit. Sampling is then done at this intermediate point.

When enclosed compressor seals are vented by means of induced draft blowers or fans, the outlet from the blower/fan can be sampled. In a previous study, a pitot tube was used to determine the air flow rate.[11] A sample of the outlet air was taken and returned to the laboratory for methane and nonmethane hydrocarbon analysis. Ambient air samples were taken around the compressor seal enclosure area at the same time and were analyzed for hydrocarbon content. The compressor seal leak rate was determined from the knowledge of air flow rate, its hydrocarbon content, and the hydrocarbon content of the ambient air.

4.3.4 Flanges

In most cases, the physical configurations of flanges lend themselves well to the determination of leak rates. For small to moderately large leaks from flanges with metal skin temperatures up to about 400°F, a narrow section of Mylar film can be used to span the open distance between the two flange faces of the leaking source. The Mylar is attached and sealed to each flange with duct tape. Connections (bulkhead fittings) for the water manometer and sampling train are attached to the Mylar.

When testing flanges with skin temperatures above 400°F, the outside perimeter of both sides of the flange connection are wrapped with asbestos insulating tape. Then, a narrow strip of aluminum foil can be used to span the opening between the flange faces. This narrow strip of material can be sealed against the asbestos tape using adjustable bands of stainless steel.

4.3.5 Relief Valves

Relief devices in gas/vapor service generally relieve to the atmosphere through a large diameter pipe which is normally located at a high point on the process unit that it serves. The "horns" can be easily bagged by placing a Mylar plastic bag over the opening and sealing it to the horn with duct tape. Because many of these devices are high above grade, accessibility to the

sampling train may be limited or prevented. It is sometimes possible to run a long piece of tubing from the outlet connection on the bag to the sampling train located at grade level or on a stable platform. And as discussed previously in the section on screening, the purpose of pressure relief devices makes them inherently dangerous to sample, especially over a long period of time. If these equipment are to be sampled for mass emissions, special care and precautions should be taken to ensure the safety of the personnel conducting the field sampling.

4.4 ACCURACY CHECKS

An accuracy check is normally performed in the laboratory by sampling an artificially induced leak rate of a known gas. This effectively points out any bias in the test methods and defines the variance component due to sampling. If the result is outside the 80 percent to 120 percent recovery range, the problem should be investigated and corrected before sampling continues. The problems and associated solutions should be noted in the test report.

4.5 ANALYTICAL TECHNIQUES

The techniques used in the laboratory analysis of the bagged samples will depend on the type of processes sampled. The following sections describe the analytical instrumentation, calibration, analytical techniques for condensate, and quality control. These are guidelines for the field sampling team and are not meant to be a detailed protocol for the laboratory personnel. Laboratory personnel should be well versed in the analysis of hydrocarbon mixtures and should design their specific analyses to the samples being examined.

4.5.1 Analytical Instrumentation

The selection of analytical instrumentation is critical to identification of individual organics in the sample. The instrument of choice depends on the type of sample being processed. Organic components of the streams of some process units may produce widely differing responses with an FID. For this reason, more comprehensive analyses by gas chromatography must be performed to identify individual components. FID gas chromatographs or electron capture gas chromatographs are commonly used to identify individual components of a sample. Other considerations besides instrument choice are the type of column used, and whether or not temperature programming is necessary to separate out

individual components of the process stream with sufficient resolution. An example of a gas chromatograph that has been used in previous studies is the Hewlett Packard 573-A Dual FID Gas Chromatograph.[12]

For some process streams such as ethylene and cumene, total hydrocarbon analyses are satisfactory. The response of the FID to these compounds is similar; therefore an instrument such as the Byron Total Hydrocarbon Analyzer (THC) can be calibrated with a single representative hydrocarbon. This instrument has an FID and resolves samples with methane and nonmethane components. The emission streams can then be analyzed for the total hydrocarbon content with reasonable accuracy.

4.5.2 Calibration

Proper calibration of both the laboratory and field instruments for the wide range of organic species is different. Each instrument must be calibrated with the appropriate species each day it is used.

Calibration of the portable hydrocarbon detector should be done with standards of hexane in air. A hexane standard of approximately 2,000 ppmv is available in a bottle supplied and certified to ± 2 percent by the manufacturer. Higher concentrations than this may lead to problems involving condensation at ambient temperatures. Lower concentrations must be generated by dilution.

The total hydrocarbon analyzer can be calibrated with the same hexane standard. The standard is related to an NBS propane standard by measuring the concentration of the NBS standard using the total hydrocarbon analyzer after the analyzer has been calibrated with the hexane standard.

The gas chromatograph is calibrated with either gas standards generated from calibrated permeation tubes containing individual VOC components or bottled standards of common gases.

4.5.3 Analytical Techniques for Condensate

Any condensate collected by the ice bath in the sampling train should be brought to the laboratory sealed in the cold trap flask. This material is transferred to a graduated cylinder to measure the volume collected. If there is enough volume to make it feasible, the organic layer should be separated from the aqueous layer (if present) and weighed to determine its density. Both the aqueous and organic phases should be analyzed by gas chromatography if water-miscible organic compounds are present.

4.5.4 Quality Control for Analytical Techniques

Blind standards should be prepared and submitted for analysis. The blind standards are prepared by diluting or mixing primary standards in a prescribed fashion so that the resulting concentrations are known. The calculated concentrations and the analytical results should be logged into a laboratory notebook. If the results are not within 25 percent of the certified level, further analyses must be performed to determine the reason. Such a procedure not only defines the analytical variance component and analytical accuracy, but it serves to point out equipment malfunctions and/or operator error before many data are affected.

SECTION 5.0
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APPENDIX A

REFERENCE METHOD 21

METHOD 21—DETERMINATION OF VOLATILE ORGANIC COMPOUND LEAKS

1. Applicability and Principle.

1.1 Applicability. This method applies to the determination of volatile organic compound (VOC) leaks from process equipment. These sources include, but are not limited to, valves, flanges and other connections, pumps and compressors, pressure relief devices, process drains, open-ended valves, pump and compressor seal system degassing vents, accumulator vessel vents, agitator seals, and access door seals.

1.2 Principle. A portable instrument is used to detect VOC leaks from individual sources. The instrument detector type is not specified, but it must meet the specifications and performance criteria contained in Section 3. A leak definition concentration based on a reference compound is specified in each applicable regulation. This procedure is intended to locate and classify leaks only, and is not to be used as a direct measure of mass emission rates from individual sources.

2. Definitions.

2.1 Leak Definition Concentration. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is present. The leak definition is an instrument meter reading based on a reference compound.

2.2 Reference Compound. The VOC species selected as an instrument calibration basis for specification of the leak definition concentration. (For example: If a leak definition concentration is 10,000 ppmv as methane, then any source emission that results in a local concentration that yields a meter reading of 10,000 on an instrument calibrated with methane would be classified as a leak. In this example, the leak definition is 10,000 ppmv, and the reference compound is methane.)

2.3 Calibration Gas. The VOC compound used to adjust the instrument meter reading to a known value. The calibration gas is usually the reference compound at a concentration approximately equal to the leak definition concentration.

2.4 No Detectable Emission. The local VOC concentration at the surface of a leak source that indicates that a VOC emission (leak) is not present. Since background VOC concentrations may exist, and to account for instrument drift and imperfect reproducibility, a difference between the source surface concentration and the local ambient concentration is determined. A difference based on meter readings of less than a concentration corresponding to the minimum readability specification indicates that a VOC emission (leak) is not present. (For example, if the leak definition in a regulation is 10,000 ppmv, then the allowable increase in surface concentration versus local ambient concentration would be 500 ppmv based on the instrument meter readings.)

2.5 Response Factor. The ratio of the known concentration of a VOC compound to the observed meter reading when measured using an instrument calibrated with the reference compound specified in the application regulation.

2.6 Calibration Precision. The degree of agreement between measurements of the same known value, expressed as the relative percentage of the average difference between the meter readings and the known concentration to the known concentration.

2.7 Response Time. The time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter.

3. Apparatus.

3.1 Monitoring Instrument.

3.1.1 Specifications.

a. The VOC instrument detector shall respond to the compounds being processed. Detector types which may meet this requirement include, but are not limited to, catalytic oxidation, flame ionization, infrared absorption, and photoionization.

b. The instrument shall be capable of measuring the leak definition concentration specified in the regulation.

c. The scale of the instrument meter shall be readable to ±5 percent of the specified leak definition concentration.

d. The instrument shall be equipped with a pump so that a continuous sample is provided to the detector. The nominal sample flow rate shall be ¼ to 3 liters per minute.

e. The instrument shall be intrinsically safe for operation in explosive atmospheres as defined by the applicable U.S.A. standards (e.g., National Electrical Code by the National Fire Prevention Association).

3.1.2 Performance Criteria.

a. The instrument response factors for the individual compounds to be measured must be less than 10.

b. The instrument response time must be equal to or less than 30 seconds. The response time must be determined for the instrument configuration to be used during testing.

c. The calibration precision must be equal to or less than 10 percent of the calibration gas value.

d. The evaluation procedure for each parameter is given in Section 4.4.

3.1.3 Performance Evaluation Requirements.

a. A response factor must be determined for each compound that is to be measured, either by testing or from reference sources. The response factor tests are required before placing the analyzer into service, but do not have to be repeated at subsequent intervals.

b. The calibration precision test must be completed prior to placing the analyzer into service, and at subsequent 3-month intervals or at the next use whichever is later.

c. The response time test is required prior to placing the instrument into service. If a modification to the sample pumping system or flow configuration is made that would change the response time, a new test is required prior to further use.

3.2 Calibration Gases. The monitoring instrument is calibrated in terms of parts per million by volume (ppmv) of the reference compound specified in the applicable regulation. The calibration gases required for monitoring and instrument performance evaluation are a zero gas (air, less than 10 ppmv VOC) and a calibration gas in air mixture approximately equal to the leak definition specified in the regulation. If cylinder calibration gas mixture are used, they must be analyzed and certified by the manufacturer to be within ±2 percent accuracy, and a shelf life must be specified. Cylinder standards must be either reanalyzed or replaced at the end of the specified shelf life. Alternately, calibration gases may be prepared by the user according to any accepted gaseous standards preparation procedure that will yield a mixture accurate to within ±2 percent. Prepared standards must be replaced each day of use unless it can be demonstrated that degradation does not occur during storage.

Calibrations may be performed using a compound other than the reference compound if a conversion factor is determined for that alternative compound so that the resulting meter readings during source surveys can be converted to reference compound results.

4. Procedures.

4.1 Pretest Preparations. Perform the instrument evaluation procedures given in Section 4.4 if the evaluation requirements of Section 3.1.3 have not been met.

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4.2 Calibration Procedures. Assemble and start up the VOC analyser according to the manufacturer's instructions. After the appropriate warmup period and zero internal calibration procedure, introduce the calibration gas into the instrument sample probe. Adjust the instrument meter readout to correspond to the calibration gas value.

NOTE.—If the meter readout cannot be adjusted to the proper value, a malfunction of the analyser is indicated and corrective actions are necessary before use.

4.3 Individual Source Surveys.

4.3.1 Type I—Leak Definition Based on Concentration. Place the probe inlet at the surface of the component interface where leakage could occur. Move the probe along the interface periphery while observing the instrument readout. If an increased meter reading is observed, slowly sample the interface where leakage is indicated until the maximum meter reading is obtained. Leave the probe inlet at this maximum reading location for approximately two times the instrument response time. If the maximum observed meter reading is greater than the leak definition in the applicable regulation, record and report the results as specified in the regulation reporting requirements. Examples of the application of this general technique to specific equipment types are:

a. Valves—The most common source of leaks from valves is at the seal between the stem and housing. Place the probe at the interface where the stem exists the packing gland and sample the stem circumference. Also, place the probe at the interface of the packing gland take-up flange seat and sample the periphery. In addition, survey valve housings of multipart assembly at the surface of all interfaces where a leak could occur.

b. Flanges and Other Connections—For welded flanges, place the probe at the outer edge of the flange-gasket interface and sample the circumference of the flange. Sample other types of nonpermanent joints (such as threaded connections) with a similar traverse.

c. Pumps and Compressors—Conduct a circumferential traverse at the outer surface of the pump or compressor shaft and seal interface. If the source is a rotating shaft, position the probe inlet within 1 cm of the shaft-seal interface for the survey. If the housing configuration prevents a complete traverse of the shaft periphery, sample all accessible portions. Sample all other joints on the pump or compressor housing where leakage could occur.

d. Pressure Relief Devices—The configuration of most pressure relief devices prevents sampling at the sealing seat interface. For those devices equipped with an enclosed extension, or horn, place the probe inlet at approximately the center of the exhaust area to the atmosphere.

e. Process Drains—For open drains, place the probe inlet at approximately the center of the area open to the atmosphere. For covered drains, place the probe at the surface of the cover interface and conduct a peripheral traverse.

f. Open-Ended Lines or Valves—Place the probe inlet at approximately the center of the opening to the atmosphere.

g. Seal System Degassing Vents and Accumulator Vents—Place the probe inlet at approximately the center of the opening to the atmosphere.

h. Access Door Seals—Place the probe inlet at the surface of the door seal interface and conduct a peripheral traverse.

4.3.2 Type II—"No Detectable Emission". Determine the local ambient concentration around the source by moving the probe inlet randomly upwind and downwind at a distance of one to two meters from the source. If an interference exists with this determination due to a nearby emission or leak, the local ambient concentration may be determined at distances closer to the source, but in no case shall the distance be less than 25 centimeters. Then move the probe inlet to the surface of the source and determine the concentration described in 4.3.1. The difference between these concentrations determines whether there are no detectable emissions. Record and report the results as specified by the regulation.

For those cases where the regulation requires a specific device installation, or that specified vents be ducted or piped to a control device, the existence of these conditions shall be visually confirmed. When the regulation also requires that no detectable emissions exist, visual observations and sampling surveys are required. Examples of this technique are:

(a) Pump or Compressor Seals—If applicable, determine the type of shaft seal. Perform a survey of the local area ambient VOC concentration and determine if detectable emissions exist as described above.

(b) Seal System Degassing Vents, Accumulator Vessel Vents, Pressure Relief Devices—If applicable, observe whether or not the applicable ducting or piping exists. Also, determine if any sources exist in the ducting or piping where emissions could occur prior to the control device. If the required ducting or piping exists and there are no sources where the emissions could be vented to the atmosphere prior to the control device, then it is presumed that no detectable emissions are present. If there are sources in the ducting or piping where emissions could be vented or sources where leaks could occur, the sampling surveys described in this paragraph shall be used to determine if detectable emissions exist.

4.3.3 Alternative Screening Procedure. A screening procedure based on the formation of bubbles in a soap solution that is sprayed on a potential leak source may be used for those sources that do not have continuously moving parts, that do not have surface temperatures greater than the boiling point or less than the freezing point of the soap solution, that do not have open areas to the atmosphere that the soap solution cannot bridge, or that do not exhibit evidence of liquid leakage. Sources that have these conditions present must be surveyed using the instrument techniques of 4.3.1 or 4.3.2.

Spray a soap solution over all potential leak sources. The soap solution may be a commercially available leak detection solution or may be prepared using concentrated detergent and water. A pressure sprayer or a squeeze bottle may be used to dispense the solution. Observe the potential leak sites to determine if any bubbles are formed. If no bubbles are observed, the source is presumed to have no detectable emissions or leaks as applicable. If any bubbles are observed, the instrument techniques of 4.3.1 or 4.3.2 shall be used to determine if a leak exists, or if the source has detectable emissions, as applicable.

4.4 Instrument Evaluation Procedures. At the beginning of the instrument performance evaluation test, assemble and start up the instrument according to the manufacturer's instructions for recommended warmup period and preliminary adjustments.

4.4.1 Response Factor. Calibrate the instrument with the reference compound as specified in the applicable regulation. For each organic species that is to be measured during individual source surveys, obtain or prepare a known standard in air at a concentration of approximately 90 percent of the applicable leak definition unless limited by volatility or explosivity. In these cases, prepare a standard at 90 percent of the saturation concentration, or 70 percent of the lower explosive limit, respectively. Introduce this mixture to the analyzer and record the observed meter reading. Introduce zero air until a stable reading is obtained. Make a total of three measurements by alternating between the known mixture and zero air. Calculate the response factor for each repetition and the average response factor.

Alternatively, if response factors have been published for the compounds of interest for the instrument or detector type, the response factor determination is not required, and existing results may be referenced. Examples of published response factors for flame ionization and catalytic oxidation detectors are included in Section 8.

4.4.2 Calibration Precision. Make a total of three measurements by alternately using zero gas and the specified calibration gas. Record the meter readings. Calculate the average algebraic difference between the meter readings and the known value. Divide this average difference by the known calibration value and multiply by 100 to express the resulting calibration precision as a percentage.

4.4.3 Response Time. Introduce zero gas into the instrument sample probe. When the meter reading has stabilized, switch quickly to the specified calibration gas. Measure the time from switching to when 90 percent of the final stable reading is attained. Perform this test sequence three times and record the results. Calculate the average response time.

5. Bibliography.

5.1 DuBose, D.A., and G.E. Harris. Response Factors of VOC Analyzers at a Meter Reading of 10,000 ppmv for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-051. September 1981.

5.2 Brown, G.E., et al. Response Factors of VOC Analyzers Calibrated with Methane for Selected Organic Compounds. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-022. May 1981.

5.3 DuBose, D.A., et al. Response of Portable VOC Analyzers to Chemical Mixtures. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Publication No. EPA 600/2-81-110. September 1981.

APPENDIX B

RESPONSE FACTORS

This appendix presents response factors estimated for a 10,000 ppmv detector reading. These response factors were previously reported in References 4 and 6. They can be used to determine whether or not a concentration is above or below 10,000 ppmv. The response factors may or may not be accurate at other concentrations.

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE

CAS No.*	Compound Name	Volatility Class	OVA				TLV			
			Response Factor		Confidence Intervals		Response Factor		Confidence Intervals	
64-19-7	Acetic acid	LL	1.64		1.11,	2.65	15.60		7.05,	46.20
108-24-7	Acetic anhydride	LL	1.39		1.09,	1.86	5.88	I	2.71,	12.80
67-64-1	Acetone	LL	0.80		0.57,	1.20	1.22		0.81,	2.00
75-86-5	Acetone cyanohydrin	HL	3.51		0.69,	>100.00	21.00	N	1.09,	>100.00
75-05-8	Acetonitrile	LL	0.95		0.85,	1.06	1.18		0.94,	1.52
98-86-2	Acetophenone	HL	18.70		5.52,	>100.00		B		
75-36-5	Acetyl chloride	LL	2.04		1.72,	2.48	2.72		1.65,	5.32
74-86-2	Acetylene	G	0.39		0.36,	0.43		B		
79-10-7	Acrylic acid	LL	4.59		3.38,	6.57		B		
107-13-1	Acrylonitrile	LL	0.97		0.80,	1.20	3.49	I	0.44,	27.90
	Allene	G	0.64		0.60,	0.69	15.00		9.68,	26.50
107-18-6	Allyl alcohol	LL	0.96		0.76,	1.27		X		
71-41-0c	Amyl alcohol, N-	HL	0.75		0.57,	1.04	2.14		0.45,	>100.00
	Amylene	LL	0.44		0.34,	0.61	1.03		0.59,	2.59
1p0-66-3	Anisole	LL	0.92		0.65,	1.46	3.91		0.52,	>100.00
100-52-7	Benzaldehyde	HL	2.46		1.38,	5.62		B		
71-43-2	Benzene	LL	0.29		0.28,	0.31	1.07		0.96,	1.20
100-47-0	Benzonitrile	HL	2.99		1.18,	15.30		B		
98-88-4	Benzoyl chloride	HL	22.10	D	3.43,	>100.00		B		
100-44-7	Benzyl chloride	HL	15.30	D	3.96,	>100.00		B		
10-86-1	Bromobenzene	L	0.40		0.34,	0.48	1.19		0.27,	>100.00
106-99-0	Butadiene, 1,3-	G	0.57		0.54,	0.60	10.90		8.11,	15.40
	Butane, N-	G	0.50		0.46,	0.55	0.63		0.58,	0.70
	Butanol, N-	LL	1.44	I	0.89,	2.34	4.11	I	2.16,	7.83
	Butanol, Sec-	LL	0.76		0.70,	0.83	1.25		0.99,	1.66
	Butanol, Tert-	S	0.53		0.38,	0.81	2.17		1.34,	4.43
106-98-9	Butene, 1-	G	0.56		0.51,	0.62	5.84		4.20,	8.89
123-86-4	Butyl acetate	LL	0.66		0.54,	0.83	1.38		1.15,	1.70
141-32-2	Butyl acrylate, N-	LL	0.70		0.63,	0.78	2.57	I	1.17,	5.68
	Butyl ether, N-	LL	2.60		0.81,	95.60	3.58	I	1.82,	7.04
	Butyl ether, Sec-	LL	0.35		0.21,	0.95	1.15		0.75,	2.17

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE (cont'd.)

CAS No.*	Compound Name	Volatility Class	OVA				TLV			
			Response Factor		Confidence Intervals		Response Factor		Confidence Intervals	
109-73-9	Butylamine, N-	LL	0.69		0.53,	0.98	2.02		1.14,	4.97
13952-84-6	Butylamine, Sec-	LL	0.70		0.58,	0.87	1.56		0.77,	5.24
75-64-9	Butylamine, Tert-	LL	0.63		0.58,	0.70	1.95		1.42,	2.91
	Butylbenzene, Tert-	HL	1.32		0.89,	2.20		B		
123-72-8	Butyraldehyde, N-	LL	1.29		1.07,	1.61	2.30		0.96,	12.80
107-92-6	Butyric acid	HL	0.80		0.38,	3.14	10.70	I	6.53,	17.60
109-74-0	Butyronitrile	LL	0.52		0.40,	0.74	1.47	I	0.62,	3.48
75-1-50	Carbon disulfide	LL		B			3.92		1.87,	12.60
	Chloroacetaldehyde	LL	9.10		5.73,	16.20	5.07		3.08,	9.79
108-90-7	Chlorobenzene	LL	0.38		0.32,	0.47	0.88		0.77,	1.00
	Chloroethane	G	5.38	I	1.87,	26.40	3.90	P	1.58,	14.10
67-66-3	Chloroform	L	9.28		5.19,	20.00		B		
25167-80-0	Chlorophenol, O-	HL	4.56		1.72,	27.20	18.30	I	6.50,	51.50
	Chloropropene, 1-	LL	0.67		0.61,	0.73	0.87		0.69,	1.16
	Chloropropene, 3-	LL	0.80		0.72,	0.90	1.24		1.08,	1.42
108-41-8	Chlorotoluene, M-	LL	0.48		0.45,	0.51	0.91		0.40,	7.47
95-49-8	Chlorotoluene, O-	LL	0.48		0.42,	0.55	1.06		0.33,	>100.00
106-43-4	Chlorotoluene, P-	LL	0.56		0.52,	0.61	1.17	I	0.77,	1.77
95-48-7	Cresol, O-	S	0.96		0.70,	1.45	4.36	I	0.40,	47.40
4170-30-0	Crotonaldehyde	LL	1.25		0.82,	2.24		B		
98-82-8	Cumene	LL	1.87		1.10,	3.71		B		
110-82-7	Cyclohexane	LL	0.47		0.39,	0.58	0.70		0.62,	0.80
108-93-0	Cyclohexanol	HL	0.85		0.65,	1.20		B		
108-94-1	Cyclohexanone	LL	1.50		0.97,	2.76	7.04		1.59,	>100.00
110-83-8	Cyclohexene	LL	0.49		0.42,	0.57	2.17		1.78,	2.74
108-91-8	Cyclohexylamine	LL	0.57		0.42,	0.86	1.38		1.28,	1.48
	Decane	HL	0.09	N	0.05,	>100.00	0.16	I	0.07,	0.35
123-42-2	Diacetone alcohol	HL	1.45		0.96,	2.48	0.98		0.44,	5.93
	Diacetyl	LL	1.54		1.25,	1.92	3.28		2.25,	5.12
	Dichloro-1-propene, 2,3-	LL	0.75		0.56,	1.09	1.75		1.14,	3.18

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE (cont'd.)

CAS No.*	Compound Name	Volatility Class	OVA			TLV		
			Response Factor	Confidence Intervals		Response Factor	Confidence Intervals	
541-73-1	Dichlorobenzene, M-	HL	0.64	0.55,	0.77	2.36	0.58,	>100.00
95-50-1	Dichlorobenzene, O-	HL	0.68	0.47,	1.11	1.26	0.35,	>100.00
	Dichloroethane, 1,1-	LL	0.78	0.62,	1.02	1.86	1.56,	2.25
107-06-2	Dichloroethane, 1,2-	LL	0.95	0.77,	1.22	2.15	1.66,	2.92
	Dichloroethylene, CIS1,2-	LL	1.27	1.05,	1.56	1.63	0.99,	3.47
	Dichloroethylene, TRANS 1,2-	LL	1.11	0.98,	1.27	1.66	0.67,	12.60
	Dichloromethane	LL	2.81	2.13,	3.87	3.85	2.46,	6.88
	Dichloropropane, 1,2-	LL	1.03	0.82,	1.33	1.65	1.06,	3.05
25167-70-8	Diisobutylene	LL	0.35	0.29,	0.44	1.41	0.96,	2.40
	Dimethoxy ethane, 1,2-	LL	1.22	0.64,	3.61	1.52	0.65,	8.38
68-12-2	Dimethylformamide, N,N-	LL	4.19	2.90,	6.58	5.29	4.05,	7.20
57-14-7	Dimethylhydrazine, 1,1-	LL	1.03	0.77,	1.45	2.70	0.51,	>100.00
67-68-5	Dimethylsulfoxide	HL	0.07 I	0.05,	0.11	8.45 I	4.15,	17.20
123-91-1	Dioxane	LL	1.48	1.04,	2.33	1.31	0.70,	3.60
106-89-8	Epichlorohydrin	LL	1.69	1.56,	1.84	2.03	1.79,	2.33
	Ethane	G	0.65	0.44,	1.58	0.69 I	0.21,	2.30
64-17-5	Ethanol	LL	1.78	1.59,	2.01	X		
	Ethoxy ethanol, 2-	LL	1.55	1.26,	1.96	1.82	0.96,	5.12
141-78-6	Ethyl acetate	LL	0.86	0.77,	0.95	1.43	1.07,	2.00
141-97-9	Ethyl acetoacetate	HL	3.82	1.89,	10.70	5.60	1.93,	38.80
140-88-5	Ethyl acrylate	LL	0.77	0.63,	0.97	X		
105-39-5	Ethyl chloroacetate	LL	1.99	1.70,	2.36	1.59	0.40,	>100.00
	Ethyl ether	LL	0.97	0.77,	1.30	1.14	0.94,	1.42
100-41-4	Ethylbenzene	LL	0.75	0.52,	1.11	4.74 D	1.38,	61.30
74-85-1	Ethylene	G	0.71	0.63,	0.82	1.56	1.26,	2.06
75-21-8	Ethylene oxide	G	2.46	1.95,	3.29	2.40	0.96,	>100.00
107-15-3	Ethylenediamine	LL	1.73	1.29,	2.46	3.26	0.78,	>100.00
64-18-6	Formic acid	LL	14.20	10.60,	19.80	B		
	Glycidol	LL	6.88	3.33,	19.70	5.66	2.08,	34.70

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE (cont'd.)

CAS No.*	Compound Name	Volatility Class	OVA Response Factor		OVA Confidence Intervals		TLV Response Factor		TLV Confidence Intervals	
	Heptane	LL	0.41	I	0.28,	0.60	0.73		0.33,	6.10
	Hexane, N-	LL	0.41		0.38,	0.45	0.69		0.63,	0.76
	Hexene, 1-	LL	0.49		0.39,	0.66	4.69	D	0.85,	>100.00
	Hydroxyacetone	LL	6.90		4.45,	12.10	15.20		6.11,	66.40
	Isobutane	G	0.41		0.29,	1.04	0.55		0.41,	0.81
115-11-7	Isobutylene	G	5.15		0.90,	38.50		B		
78-79-5	Isoprene	LL	0.59		0.46,	0.80		X		
67-63-0	Isopropanol	LL	0.91		0.72,	1.20	1.39		0.94,	2.31
108-21-4	Isopropyl acetate	LL	0.71		0.62,	0.83	1.31		1.04,	1.72
75-29-6	Isopropyl chloride	LL	0.68		0.60,	0.77	0.98		0.82,	1.22
	Isovaleraldehyde	LL	0.64		0.57,	0.74	2.19	D	1.14,	6.65
141-79-7	Mesityl oxide	LL	1.09		0.94,	1.29	3.14		1.43,	12.00
	Methacrolein	LL	1.20		0.90,	1.71	3.49	D	1.51,	19.80
79-41-4	Methacrylic acid	HL	0.82		0.31,	14.70	1.06	I	0.24,	4.56
67-56-1	Methanol	LL	4.39	P	3.61,	5.60	2.01		1.66,	2.48
	Methoxy-ethanol, 2-	LL	2.25		1.62,	3.34	3.13		1.13,	27.40
79-20-9	Methyl acentate	LL	1.74		1.46,	2.13	1.85		1.44,	2.49
	Methyl acetylene	G	0.61		0.58,	0.64	6.79		4.86,	10.40
74-87-3	Methyl chloride	G	1.44		1.22,	1.76	1.84		0.73,	>100.00
78-93-3	Methyl ethyl ketone	LL	0.64		0.51,	0.84	1.12		0.93,	1.38
107-31-3	Methyl formate	LL	3.11		2.42,	4.14	1.94		1.72,	2.21
80-62-6	Methyl methacrylate	LL	0.99		0.90,	1.10	2.42		1.39,	5.38
	Methyl-2-pentanol, 4-	LL	1.66		1.27,	2.32	2.00		1.40,	3.15
	Methyl-2-pentanone, 4-	LL	0.56		0.46,	0.69	1.63		1.22,	2.35
	Methyl-3-butyn-2-OL, 2-	LL	0.59		0.44,	0.86		X		
	Methylal	LL	1.37		1.06,	1.83	1.46		1.24,	1.74
100-61-8	Methylaniline, N-	HL	4.64		3.91,	5.57	9.46		2.55,	35.20
108-87-2	Methylcyclohexane	LL	0.48		0.28,	1.39	0.84		0.68,	1.09
	Methylcyclohexene, 1-	LL	0.44		0.36,	0.54	2.79		1.79,	5.12

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE (cont'd.)

CAS No.*	Compound Name	Volatility Class	OVA Response Factor		OVA Confidence Intervals		TLV Response Factor		TLV Confidence Intervals	
77-75-8	Methylpentynol	LL	1.17		0.71,	2.48	3.42		1.83,	8.54
98-83-9	Methylstyrene, A-	LL	13.90		9.50,	21.50		B		
110-91-8	Morpholine	LL	0.92		0.67,	1.40	2.59	I	0.64,	10.50
98-95-3	Nitrobenzene	ML		B			0.01	I	0.00,	82.80
79-24-3	Nitroethane	LL	1.40		1.20,	1.65	3.45		1.56,	13.00
75-52-5	Nitromethane	LL	3.52		3.03,	4.15	7.60		1.91,	>100.00
25332-01-4	Nitropropane	LL	1.05		0.80,	1.48	2.02		1.17,	4.47
	Nonane-N	LL	1.54		0.94,	2.98	11.10		3.13,	>100.00
	Octane	LL	1.03		0.89,	1.21	2.11		1.68,	2.75
109-66-0	Pentane	LL	0.52		0.42,	0.66	0.63		0.57,	0.70
	Picoline, 2-	LL	0.43		0.38,	0.50	1.18		1.08,	1.29
	Propane	G	0.55	I	0.46,	0.72	0.60	P	0.59,	0.69
123-38-6	Propionaldehyde	LL	1.14		1.00,	1.32	1.71		1.11,	3.06
79-09-4	Propionic acid	LL	1.30		1.03,	1.70	5.08	D	0.73,	>100.00
71-23-8	Propyl alcohol	LL	0.93		0.77,	1.16	1.74		1.06,	3.50
	Propylbenzene, N-	LL	0.51		0.45,	0.58		B		
115-07-1	Propylene	G	0.77		0.44,	2.66	1.74	I	0.15,	20.30
75-56-9	Propylene oxide	LL	0.83		0.74,	0.95	1.15		0.69,	2.46
110-86-1	Pyridine	LL	0.47		0.40,	0.55	1.16		1.03,	1.34
100-42-5	Styrene	LL	4.22		3.45,	5.27		B		
79-34-5c	Tetrachloroethane, 1,1,1,2-	LL	4.83	D	1.24,	>100.00	6.91		3.14,	22.50
	Tetrachloroethane, 1,1,2,2-	LL	7.89		5.01,	13.80	25.40		8.06,	>100.00
	Tetrachloroethylene	LL	2.97		1.71,	6.11		B		
108-88-3	Toluene	LL	0.39		0.36,	0.43	2.68	D	0.79,	>100.00
	Trichlorobenzene, 1,2,4-	ML	1.21	I	0.50,	2.94	0.47	I	0.32,	0.68
71-55-6	Trichloroethane, 1,1,1-	LL	0.80		0.72,	0.90	2.40		1.81,	3.35
79-00-5	Trichloroethane, 1,1,2-	LL	1.25		1.05,	1.50	3.69		2.77,	5.16
79-01-6	Trichloroethylene	LL	0.95		0.83,	1.09	3.93		2.68,	6.32
96-18-4	Trichloropropane, 1,2,3-	LL	0.96		0.64,	1.78	1.99		1.27,	3.82

TABLE B-1. RESPONSE FACTORS WITH 95% CONFIDENCE INTERVALS ESTIMATED AT 10,000 PPMV RESPONSE (cont'd.)

CAS No.*	Compound Name	Volatility Class	OVA Response Factor		OVA Confidence Intervals		TLV Response Factor		TLV Confidence Intervals	
121-44-8	Triethylamine	LL	0.51		0.40,	0.70	1.48		0.96,	2.76
108-05-4	Vinyl acetate	LL	1.27		0.95,	1.82	5.91	D	1.26,	>100.00
75-01-4	Vinyl chloride	G	0.84		0.61,	1.38	1.06		0.59,	4.60
	Vinyl propionate	LL	1.00	I	0.57,	1.74	1.21	I	0.46,	3.20
75-35-4	Vinylidene chloride	LL	1.12		0.87,	1.52	2.41		1.82,	3.35
106-42-3	Xylene, P-	LL	2.12		1.71,	2.68	7.87		3.49,	24.90
	Xylene, M-	LL	0.40		0.36,	0.46	5.87	D	0.91,	>100.00
95-47-6	Xylene, O-	LL	0.43		0.28,	0.85	1.40		0.61,	9.33

*CAS numbers refer to the Chemical Abstracts Registry numbers of specific chemicals, isomers, or mixtures of chemicals.

G = Gas; LL = light liquid; HL = heavy liquid

I = inverse estimation method

D = possible outliers in data

N = narrow range of data

X = no data available

B = 10,000 ppmv response unachievable

P = suspect points eliminated

TABLE B-2. TESTED COMPOUNDS WHICH APPEAR TO BE UNABLE TO ACHIEVE AN INSTRUMENT RESPONSE OF 10,000 PPMV AT ANY FEASIBLE CONCENTRATION

Instrument[a]	OVA		TLV
CAS[b]	Compound Name	CAS[b]	Compound Name
--	Acetyl-1-propanol, 3-	98-86-2	Acetophenone
75-1-50	Carbon disulfide	--	Acetyl-1-propanol, 3-
56-23-5	Carbon tetrachloride	74-86-2	Acetylene
--	Dichloro-1-propanol, 2,3	79-10-7	Acrylic acid
--	Dichloro-2-propanol, 1,3	100-52-7	Benzaldehyde
--	Diisopropyl benzene, 1,3	100-47-0	Benzonitrile
--	Dimethylstyrene, 2,4	98-88-4	Benzoyl chloride
1221	Freon 12	100-44-7	Benzyl chloride
98-01-1	Furfural	--	Butylbenzene, Tert-
--	Methyl-2,4-pentanediol,2	56-23-5	Carbon tetrachloride
1660	Monoethanolamine	67-66-3	Chloroform
98-95-3	Nitrobenzene	4170-30-0	Crotonaldehyde
108-95-2	Phenol	98-82-8	Cumene
--	Phenyl-2-propanol, 2-	108-93-0	Cyclohexanol
		--	Dichloro-1-propanol, 2,3
		--	Dichloro-2-propanol, 1,3
		--	Diisopropyl benzene, 2,4
		--	Dimethylstyrene, 2,4
		64-18-6	Formic acid
		1221	Freon 12
		98-01-1	Furfural
		115-11-7	Isobutylene
		--	Methyl-2,4-pentanediol
		98-83-9	Methylstyrene, A-
		1660	Monoethanolamine
		108-95-2	Phenol
		--	Phenyl-2-propanol, 2-
		--	Propylbenzene, N-
		100-42-05	Styrene
		2860	Tetrachloroethylene

[a]OVA and TLV are two portable hydrocarbon analyzers that have been used in previous studies of fugitive emissions. Operating with a flame ionization detector (FID), OVA measures nonmethane hydrocarbon emissions; TLV measures total hydrocarbon emissions.

[b]CAS numbers refer to the Chemical Abstracts Registry numbers of specific chemicals, isomers, or mixtures of chemicals.

APPENDIX C

CALCULATION OF MASS EMISSION RATES

APPENDIX C

The calculation of emission rates is illustrated below for VOC:

$$E_T = E_V + E_L$$

where E_T = total VOC emission rate, lb/hr,

E_L = condensed organic liquid component of the VOC emission rate, lb/hr, and

E_V = vapor component of the VOC emission rate, lb/hr.

The emission rate of the vapor component is calculated from the following equation:

$$E_V = K \frac{QPM_A (C_s - C_a)}{T}$$

where $K = 5.6 \times 10^{-6}$, a factor incorporating conversion factors and standard temperature and pressure,

Q = flow rate of gas through the sample train, actual cubic feet/minute,

P = sampling system pressure at the dry gas meter, psia,

M_A = molecular weight of the air/VOC mixture,

C_s = concentration of VOC in the gas sample from the sampling train, ppm by weight,

C_a = concentration of VOC in the ambient air, ppm by weight, and

T = sampling system temperature at the dry gas meter, ^{o}R.

The emission rate of the organic condensate component, E_L, is determined from the following equation:

$$E_L = \frac{0.1\ V}{t}$$

where E_L = organic condensate rate, lb/hr,
V = volume of condensate collected, ml, and
t = time over which the sample was collected, min.

This calculation assumes an average density of 0.75 g/cc for the organic condensate.

These equations can be modified as necessary to provide for water-miscible compounds and to express emissions in terms of compounds other than hexane.

APPENDIX D

LEAK RATE/SCREENING VALUE EQUATIONS

TABLE D-1. PREDICTION EQUATIONS FOR NONMETHANE LEAK RATE FOR VALVES, FLANGES, AND PUMP SEALS IN SOCMI PROCESSES

SOURCE TYPE	INSTRUMENT	LEAST - SQUARES EQUATION[c]	NUMBER OF DATA PAIRS	CORRELATION COEFFICIENT (r)	STANDARD DEVIATION OF ESTIMATE
Valves[a]					
Gas Service	OVA	$NMLK = 1.68\ (10^{-5})\ (MXOVA)^{0.693}$	99	0.66	0.716
Light Liquid Service	OVA	$NMLK = 3.74\ (10^{-4})\ (MXOVA)^{0.47}$	129	0.47	0.902
Flanges[b]	OVA	$NMLK = 3.731\ (10^{-5})\ (MXOVA)^{0.82}$	52	0.77	0.520
Pump Seals[a]	OVA	$NMLK = 1.335\ (10^{-5})\ (MXOVA)^{0.898}$	52	0.81	0.650

NMLK = Nonmethane leak rate (lb/hr)
MXOVA = Maximum screening value (ppmv) - OVA instrument

[a]Source: Langley, G. J., and R. G. Wetherold (Radian Corporation) 1981. Evaluation of Maintenance for Fugitive VOC Emissions Control. EPA-600/52-81-080. pp. 54-56.

[b]Source: Wetherold, R.G., L.P. Provost, and C.D. Smith (Radian Corporation). Assessment of Atmospheric Emissions from Petroleum Refining: Volume 3. Appendix B. (Prepared for U.S. Environmental Protection Agency.) Research Triangle Park, North Carolina. Publication No. EPA-600/2-80-075c.

[c]NMLK is given in units of lb/hr. The units may have to be changed for reporting purposes.

APPENDIX E

SELECTION OF SAMPLE SIZE FOR FLANGE SCREENING

APPENDIX E

SELECTION OF SAMPLE SIZE FOR SCREENING FLANGES AND OTHER CONNECTORS

In estimating emissions for a given process unit, all equipment components must be surveyed for each class of components. For example, all valves in gas/vapor service must be screened to establish the number of components in each of the given ranges of screening values. The one exception to this "total component screening" criterion is the category of flanges and other connectors. In typical process units, flanges and other connectors represent the largest count of individual equipment components, making it costly to screen all components. The purpose of this appendix is to present a methodology for determining how many flanges or other connectors must be screened to constitute a large enough sample size to identify the actual screening value distribution of flanges and other connectors in the entire process unit. Please note that the sampling is to be a random sampling throughout the process unit.

The basis for selecting the sample population to be screened is the probability that at least one "leaking" flange will be in the screened population. The "leaker" is used as a representation of the complete distribution of screening values for the entire class of sources. The following binomial distribution was developed to approximate the number of flanges and other connectors that must be screened to ensure that the entire distribution of screening values for these components is represented in the sample:

$$n \geq N * [1 - (1 - p)^{1/D}] \qquad \text{(E-1)}$$

where D may be taken as (fraction of leaking flanges) * N and $p \geq 0.95$.

Currently available data gathered for flanges in VOC service in chemical process units show an estimated 2.09 percent flanges leaking. The EPA recommends starting with the factor 0.0209 for the fraction of leaking flanges, since the actual leak frequency for flanges in a chemical process unit probably will not be known prior to the selection of a sample size for screening. A larger sample size will be required for units exhibiting a lower fraction of leaking flanges and other connectors. If a lower leak frequency

for a process unit is known or can be estimated, it may be substituted into the equation above in place of 0.0209.

After 'n' flanges have been screened, an actual leak frequency should be calculated as follows:

$$\text{Leaking Frequency} = \frac{\text{Number of leaking flanges}}{n} \qquad \text{(E-2)}$$

Then, the confidence level of the sample size can be calculated using the following equation, based upon a hypergeometric distribution:

$$P = 1 - \frac{(N-D')!\ (N-n)!}{N!\ (N-D'-n)!} \qquad \text{(E-3)}$$

where N = Total population of flanges and other connectors

n = Sample size

$$D' = \frac{\text{Number of leaking flanges and connectors}}{n} * N$$

If 'p' calculated in this manner is less than 0.95, then a less than 95 percent confidence exists that the screening value distribution has been properly identified. Therefore, additional flanges/connectors must be screened to achieve a 95 percent confidence level. The number of additional flanges required to satisfy the requirement for a 95 percent confidence level can be calculated by solving Equation (E-1) again, using the leak frequency calculated in Equation (E-2), and subtracting the original sample size. After this additional number of flanges/connectors have been screened, the revised fraction of leaking components and the confidence level of the new sample size (i.e., the original sample size plus the additional flanges/connectors screened) should be recalculated using Equation (E-3). The Agency requires sufficient screening to achieve a 95 percent confidence level, until a maximum of 50 percent of the total number of flanges and other connectors in the process unit have been screened. The EPA believes that 50 percent of the total flange/connector population is a reasonable upper limit for a sample size. If half of the total number of flanges and other connectors are screened, no further flange screening is necessary, even if a 95 percent confidence level has not been achieved.

APPENDIX F

DETERMINATION OF EMISSION RATES FOR DEFAULT ZERO SCREENING VALUES

In developing emission estimates using correlations, the emissions associated with zero screening values are estimated using default emission rates. Due to their logarithmic form, the correlations estimate zero emissions for zero screening values. Field testing, however, indicates that there are finite emissions associated with equipment screening at the background concentrations. To account for these emissions in the protocol, EPA has established some default zero screening values and their associated emission rates based on data gathered during the SOCMI Maintenance Study.

Twelve data pairs for valves in gas/vapor service were bagged to determine mass emissions during the Maintenance Study. The mass emission rates for these twelve sources were averaged to establish the emission rate for gas/vapor valves screening at 0 ppm above the background level. This average emission rate is 0.000033 kilograms per hour per source. Using the SOCMI/OVA correlation for gas/vapor valves shown in Appendix D and this emission rate, the "default zero" screening value was established (8 ppm). All components screening at or below this default screening value are assumed to have an emission rate equal to the default zero emission rate.

No mass emissions data for zero screening values were available for equipment components other than valves in gas/vapor service. The default zero emission rates for all equipment types and services were established using the correlations shown in Appendix D and the default zero screening value (8 ppm) calculated from the gas/vapor valves bagging data.

Equipment Type/Service	"Default Zero" Screening Value, ppm	Zero Screening Value Emission Rate (kg/hr/source)
Valves, gas	8	0.000033
Valves, light liquid	8	0.000451
Flanges	8	0.000093
Pumps and all other components	8	0.000039

APPENDIX G

DEVELOPMENT OF A DEFAULT EMISSION RATE FOR EQUIPMENT THAT DOES NOT SCREEN ABOVE THE BACKGROUND CONCENTRATION

Text adapted from Guidance for Estimating Fugitive Emissions, published by the Chemical Manufacturers Association.

APPENDIX G

DEVELOPMENT OF A DEFAULT EMISSION RATE FOR EQUIPMENT THAT DOES NOT SCREEN ABOVE THE BACKGROUND CONCENTRATION.

If bagging data for equipment components that do not screen above background do not exist, the EPA default emission rates in Appendix F should be used to estimate emissions from these sources. If a process unit intends to develop its own default zero emission rates, it must bag samples from each equipment type (e.g., gas/vapor valves, light liquid valves) for which it plans to determine default zero emission rates. If bagging data exist, the first step in developing a default emission rate is to adjust for the background concentration by subtracting the background bag from the source bag; that is, calculate

$$X_i = LR_{s,i} - LR_{B,i}$$

where $LR_{s,i}$ = leak rate from source bag i

$LR_{B,i}$ = leak rate from background bag i

Next, take the logarithm of the data and add a constant (if necessary) to avoid taking the logarithm of a nonpositive X_i. The following procedure is used:

Case 1: If all of the data are positive, $y_i = \log(Xi)$

Case 2: If all of the data are nonnegative with at least one zero,

$$y_i = \log(Xi + C)$$

where C = largest power of 10 less than the smallest nonzero value of X (e.g., if the smallest nonzero value of X is 8×10^{-4}, then $C = 1 \times 10^{-4}$).

Case 3: If some of the data are negative, the smallest value (K1) is first subtracted from each observation in the data set (note that K1 is a negative number). This results in all nonnegatives, with at least one zero value. Then K2 is added to each observation in the set, where K2 = largest power of 10 less than the smallest nonzero value of the updated nonnegative data set. Hence, the logarithmic expression used is

$$y_i = \log(Xi + C) \quad \text{where } C = K2\text{-}K1$$

The average, standard deviation, and scale bias correction factor (SBCF) are calculated for the Y_i as follows:

$$\bar{y} = \frac{1}{n} \sum_{i=1}^{n} y_i$$

$$S^2 = \frac{1}{n-1} \sum_{i=1}^{n} (y_i - \bar{y})^2$$

$$SBCF = g\,[(\ln 10)^2\,(S^2/2)]$$

where $g(t) = 1 + \frac{(n-1)}{n}\,t + \frac{(n-1)^3 t^2}{n^2 2!(n+1)} + \frac{(n-1)^5 t^3}{n^3 3!(n+1)(n+3)} + \ldots$

(Approx. 10-15 terms required to obtain accuracy of $+ 10^{-7}$)

The estimate of emissions for components screening below the lower limit of detection (LLD) for the screening instrument, (EF_{1*}), is then:

$$EF_1{}^* = \max\,[(10^{\bar{y}} SBCF) - C,\ \emptyset]$$

where $C = \emptyset$ for Case 1, and previously stated for Case 2 and Case 3.

A statistical test is used to compare the calculated EF_{1*} with the established 'default zero' in Appendix F. The results of this test determine which value (EF_{1*} or 'default zero') is used to represent emissions for components screening below the LLD. The test involves two cases:

Case A: If EF_{1*}<'Default zero', then use EF_{1*} if

$$EF_{UL} = 10^{\bar{y}+t(.95,\ n-1)\sqrt{s^2/n}} \qquad \text{SBCF} < \text{'Default zero'}$$

(Use 'Default zero' if $EF_{UL} \geq$ 'Default zero')

Case B: If EF_{1*} > 'Default zero', then use EF_{1*} if

$$EF_{LL} = 10^{\bar{y}-t(.95,\ n-1)\sqrt{s^2/n}} \qquad \text{SBCF} > \text{'Default zero'}$$

(Use 'Default zero' if $EF_{LL} \leq$ 'Default zero')

A confidence interval for EF_1 can be calculated as:

$$(10^{\bar{y}+t_1(.975,\ n-1)\sqrt{s^2/n}} \text{ SBCF},\ 10^{\bar{y}+t_1(.975,\ n-1)\sqrt{s^2/n}} \text{ SBCF})$$

Note: This interval should only involve the nonnegative region. In the case where the above computation includes negative values, it should be truncated to zero.

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Project Officer is David Markwordt, MD-13, (919) 541-0837

16. ABSTRACT

EPA has developed a Protocol for Generating Unit-Specific Emission Estimates fir Equipment Leaks of VOC and VHAP. The protocol provides several methods for estimating emissions from equipment leaks. These methods range from the application of average emission factors for the equipment component inventory to the use of bagging data for generating unit-specific leak rate/screening value correlations. In addition, the protocol provides technically sound methods of source screening and mass emissions sampling (bagging). The document will help facitilies generate accurate plant-specific equipment leak emissions.

17. KEY WORDS AND DOCUMENT ANALYSIS

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